UNIVERSITY OF
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Chromatic Monitoring of Sulphurhexaflouride using Mass Spectrometry

Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy

by

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Abstract

Modern day Circuit Breakers use Sulphurhexaflouride (SF_6) as a background gas due to its insulation properties and excellent arc-quenching properties. However, leaks occur, which can be expensive and also toxic and hazardous to the environment. Some type of monitoring tool would prove to be useful and widely appreciated in the power industry. This thesis explores the possibility of using a monitoring system to check for SF_6 leaks using the measurement capabilities of the mass spectrometer and the functionality of a technique called tri stimulus chromaticity. Atomic mass spectrum data (124-130 AMU) is subject to chromatically based data analysis techniques in order that concentrations of SF_6 in air of below 100 parts per billion may be detected by identifying emerging patterns in mass spectra using triangle filters. These methods are shown to provide a fast and simple indication of SF_6 presence which is better than human interpretation of raw data. A mass spectrometer tri-measurement system is developed which makes use of the chromatic method to strategically position measurement points to locate positions of single SF_6 leaks within a 2 and a 3 dimensional space. This is achieved by building up a physical profile of the position using H-s and H-L polar plots. This project shows how the ideas and techniques of chromatic monitoring can be transferred and used in the spatial and atomic mass domains to improve SF_6 detection capability within confined areas.

Acknowledgments

Firstly, I would like to thank my supervisor, Prof. J. Spencer for his continual guidance, encouragement and ideas throughout the whole process of this project. I also owe thanks also to experimental officer Mr. J Humphries for his assistance in the laboratory. I would also like to thank all of the members of the "Centre for Intelligent Monitoring Systems" at the University of Liverpool for all of their continual help, encouragement and friendship.

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Chapter 1 – Introduction

This Chapter introduces and reviews circuit breakers and the context in which they are used. It contains a description of power systems and circuit breakers, and it gives a brief history of how they have evolved into the modern day Sulphurhexaflouride filled circuit breakers and highlights some of the other techniques that have been used for current interruption. The aim of the project is also outlined with an explanation of why it is important to try and design some type of system to provide a cost effective wide area monitoring system for the detection of SF_6 leaks. There is also a section which gives a brief description of each Chapter to assist in the reading of the thesis.

1.1 Introduction

Around 600 BC the Greeks found that by rubbing an 'electron' (a hard Fossilised resin that today is known as Amber) against a fur cloth, it would attract particles of straw. This strange effect remained a mystery for over 2000 years, until, around AD 1600, when Dr William Gilbert investigated the reactions of amber and magnets and first recorded the word 'Electric' in a report on the theory of magnetism. Gilbert's experiments led to a number of investigations by many pioneers in the development of electrical technology over the next 350 years,

Redwood Kardon [1]. Today the modern world relies entirely on the supply of electricity.

The purpose of a power system is to transport and distribute the electrical energy generated in power plants to the consumer in a safe and reliable way, *Lou Van der Sluis* [2] . These power systems contain multiple components one of which is the circuit breaker, which is a protection device designed to protect the system from failures occurring such as lightening strikes and short circuits. Unlike a fuse which operates once and then has to be replaced, a circuit breaker can be reset (either manually or automatically) to resume normal operation. Under short-circuit conditions a current of many times greater than normal load current can flow, and when a circuit breaker tries to interrupt this current an arc forms between the open contacts allowing the flow of current to continue. Circuit breakers incorporate features to divide and extinguish the arc. In air-insulated and miniature circuit breakers a structure consisting of metal plates or ceramic ridges usually cools the arc when it is driven against them due to the resultant Lorentzian forces. Larger circuit breakers may use vacuum, an inert gas such as Sulphurhexaflouride or have contacts immersed in oil to suppress the arc.

1.2 History

SF_6 gas filled circuit breaker technology is the latest in the evolution of a series of technologies for circuit breaking. The quick-break fire knife switch has been described as probably the first circuit breaker. It was recorded that such switches were "without any formal control other than that provided by the switch attendant who, armed with an insulated hatchet, was invited to chop the arc in two", *Flurscheim* [3]. The limitations of the knife prompted an unknown inventor to take the surprising step of immersing the device in flammable transformer oil. However, this proved to be an effective move resulting in the inception of the oil circuit breaker and the beginning of circuit breaker development, *Isaac* [4].

Circuit breakers have continued to evolve over the decades. There have been many developments in oil and air blast circuit breakers including for example the double pressure blast type circuit breaker and the "puffer" type to name just two. However, the discovery of Sulphurhexaflouride (SF_6) as being an excellent arc quenching medium in the 1950's transformed the development of switchgear. Oil, air and vacuum can compete with SF_6 at distribution levels, but for transmission voltage ($\geq$132kV) SF_6 is by far the most popular, *Isaac* [4]. Unfortunately, SF_6 is a greenhouse gas, *Telfer* [5], and for this reason there are still environmental concerns with its use.

There have been developments to try to improve circuit breaker operation so that a non-SF_6 breaker can compete with an SF_6 insulated type. These include techniques such as:

- PTFE ablation. This technique involves constructing a nozzle made out of PTFE (polymer consisting of recurring tetrafluorethylene monomer units) *Sillars* [6]. PTFE is an electrical insulating material with very good electrical (high resistance) and dielectric properties at low electromagnetic frequencies. PTFE is exposed to an electric arc causing it to ablate creating a insulating medium at the source of the arc which helps improve performance. Its broad application and at different temperature ranges and its ductility are other advantages of PTFE *Ali.*[7].

- Electromagnetic Arc Control. This involves using a magnetic field produced by a current through a coil to manipulate the arc in order to achieve better arc quenching in Vacuum and therefore eliminate the need for SF_6. *Shpanin* [8].

However a commercial circuit breaker has yet to be designed that can compete with one that uses SF_6 and there is no single superior environmentally friendly gas available to replace it. Therefore it looks like SF_6 will continue to be used for the immediate future.

1.3 Project Aim

Modern day circuit breakers contain SF_6 and due to environmental conditions, general wear and tear and human error, SF_6 can leak from such devices. In the US alone, leak detection surveys have noted that approximately 10 percent of circuit breaker populations may leak, and of these leaking populations, 15 percent of the breaker leaks were minor, with repairs that could be conducted immediately, while the remaining 85 percent were considered significant and had to be referred to operations for scheduled repairs, *Blackman* [9]. This can be expensive and detrimental to the environment; therefore some type of monitoring system to detect and locate leaks would prove to be useful and may be attractive to the power industry. Currently there are no practical systems capable of cost effectively continuously monitoring for SF_6 leaks over a large area. To date the accepted way of detecting a leak has been to check the pressure gauge of a system over a long time (a reduction in pressure implies a loss in gas). The problem with this is that it could take months before a leak is detected and by then a significant amount of gas will have leaked from the system. This method is also open to human error (e.g. forgetting to check, noting wrong pressure, temperature variations etc.). After determining that there is a leak present, it is very difficult to locate it. If the system is large it can be a huge task trying to find an SF_6 leak as the gas is odourless and colourless. In addition, there may be more than one leak which would be highly likely in a large system.

There have been techniques developed for detecting SF_6 leaks such as laser camera technology, but this is very expensive. Therefore, this project aims to develop a more efficient monitoring technique using a residual gas analyser (RGA) for wide area monitoring.

This thesis covers the application of chromatic monitoring techniques in the atomic mass unit and space domains. Chromatic transformations have been used in colour science to transform information into mathematical forms that can emphasize and distinguish particular information. There has been a considerable amount of work undertaken by colour scientists (e.g. Levkowitz and Herman, 1993; Rogers, 1985). It is therefore advantageous to build upon such a wealth of knowledge in developing the concepts of chromaticity, *Jones* [10].

The chromatic methodology is based upon comparisons, which are translated into mathematical cross correlations. Because it is quantative in nature, it enables numerical scales of judgment to be established. However unlike methodologies such as neural networks, it has a high degree of traceability, lends itself to a hierarchical approach to different levels of detailed information, and significantly enables the quantified information to be easily assimilated via patterns so that in-depth mathematical knowledge is not mandatory, *Jones* [10]

1.4 Thesis Organisation

Chapter 2

This Chapter gives a review of the circuit breaker and of Sulphurhexaflouride. A list is given of the different applications for which SF_6 has been used and of the complications that arise from using this gas. The mass spectrometer used to detect and analyse gas samples is introduced and a review is given on the history and operation of it. The theory of gas dispersion and Chromaticity is reviewed and it is shown how chromatic methods can be used in domains other than the colour domain.

Chapter 3

This Chapter describes how gas samples are prepared and obtained, it is also explained how the mass spectrometers are used to obtain data. Typical background mass spectra are analysed and each peak is identified. An "ideal" ambient scan is constructed and it is shown how gas samples can be isolated for analysis.

Chapter 4

This Chapter reports results taken using both the RGA300 (onsite in Holland) and the CIRRUS (Laboratory tests). The onsite tests consist of mass spectrums taken near simulated SF_6 leaks at the test station and on actual leaks in a power station. The laboratory tests consist of simulated leaks of known quantities inside a 2 dimensional and 3 dimensional space

Chapter 5

This Chapter is concerned with chromatic analysis techniques and interpretation of results to yield a better understanding of the systems' behaviour. The tests performed in Chapter 4 are analysed based on chromatic processing both in chromatic RGB and HLS domains. H-L and H-S plots are presented and discussed.

Chapter 6

This chapter draws together the conclusions of each section regarding the experimental results and analysis and presents them in the form of general discussion looking at different techniques that were utilised throughout this project. A summary of the implications of the analysis presented in this thesis is given with suggestions of further research for the future.

1.5 References

[1] Redwood Kardon, *History of Wiring* http://www.codecheck.com/pp_elect.html ©1998

[2] Lou Van der Sluis, *Transients in Power Systems*, John Wiley & sons Ltd. 2001, pp1

[3] C. H. Flurscheim, *Development in power Engineering*, Proc. IEE, 112, No.1, January, pp5-12,, 1965

[4] L. T. Isaac, Puffer circuit breaker diagnostics using novel optical fibre sensors Ph.D. Thesis, 1997: pp1

[5] D. J. Telfer, J. Humphries, J. W. Spencer, G. R. Jones, *Influence of PTFE on arc quenching in an experimental self-pressurised circuit breaker*, GD2002 XIV International conference on gas discharges & applications: pp91-94

[6] R. W. Sillars (1973), *Electrical insulating materials and their application.* IEE Monograph Series 14, UK, Billing & Sons Ltd., pp137-179.

[7] S. M. G. Ali (1-6 July 2001), *Switch Gear Design, Development and Service.* High Voltage Engineering and Testing, University of Northumbria at Newcastle, Ninth International School, pp286-318.

[8] L. Shpanin (2006), *Electromagnetic Arc Control for Current Interruption*, The University of Liverpool, Ph.D. Thesis.

[9] J. Blackman, M. Averyt, *SF_6 Leak Rates from High Voltage Circuit Breakers – U.s. EPA Investigates Potential Greenhouse Emissions Souce*, Document produced for the US Environmental Protection Agency, Available Online, 2008: http://www.epa.gov/electricpower-sf6/documents/leakrates_circuitbreakers.pdf

[10] G.R. Jones, A. G. Deakin, J. W. Spencer, *Chromatic Monitoring of Complex Conditions*, CRC Press, Taylor & Francis, 2005

Chapter 2 – Theory and background

This Chapter gives a review of the circuit breaker and of Sulphurhexaflouride. A list is given of the different applications for which SF_6 has been used and of the complications that arise from using this gas. The mass spectrometer used to detect the gas is introduced and a review is given on the history and operation of it. The theory of gas dispersion and Chromaticity is reviewed and it is shown how chromatic methods can be used in domains other than the colour domain.

2.1 The circuit breaker

This project concentrates on the detection of leaks from circuit breakers. Figure 2-1 shows a 3-phase SF_6 type dead tank high voltage circuit breaker.

Figure 2-1: Typical Circuit breaker, *Siemens* [1]

Current enters and leaves the breaker through cables or wires terminating on the top of the insulator bushings. The horizontal cylindrical tanks contain the interrupters which operate in an envelope filled with sulphur hexafluoride (SF_6) gas. The control cabinet for the breaker is on the left side of the unit, which contains the mechanism that opens and closes all three poles phases at the same time. Unlike smaller breakers used in low voltage systems, the over-current sensing relays are always separately mounted in this form of breaker.

It would be unpractical and unsafe to undertake lots of tests on a live circuit breaker. For the purposes of this project initial tests were undertaken in the

laboratory with a number of different systems to obtain data that can be analysed and used to refine the detection system. The following sections give a description of the different test systems and initial sites.

2.1.1 Gas Vessel

A section of a real circuit breaker was modified and used as a small gas vessel so that it can be filled with SF_6 and used to simulate a leak in laboratory conditions and for quantifying the amount of gas leakage, Figure 2-2. The maximum pressure that the cell can withstand is approximately 3 Bar.

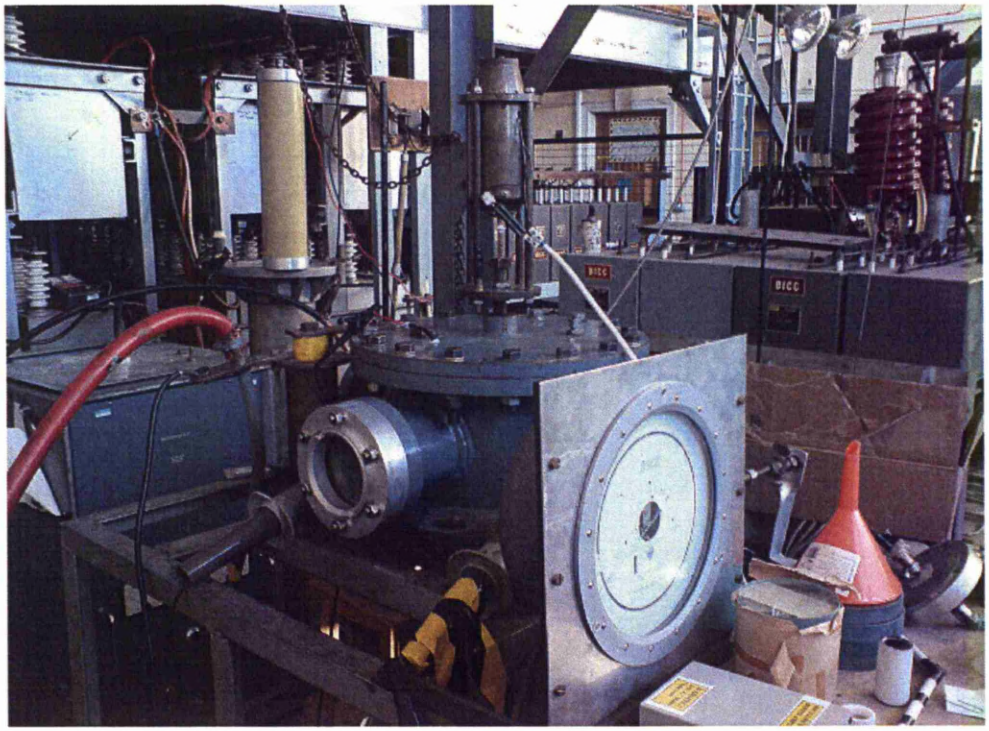


Figure 2-2: Cell used for SF_6 tests

2.1.2 Industry Tests

Tests were performed on "Live" circuit breakers at a 150 kV SF_6 gas insulated substation in Holland and at KEMA's high power test labs in Arnhem, Holland, Figure 2-3.

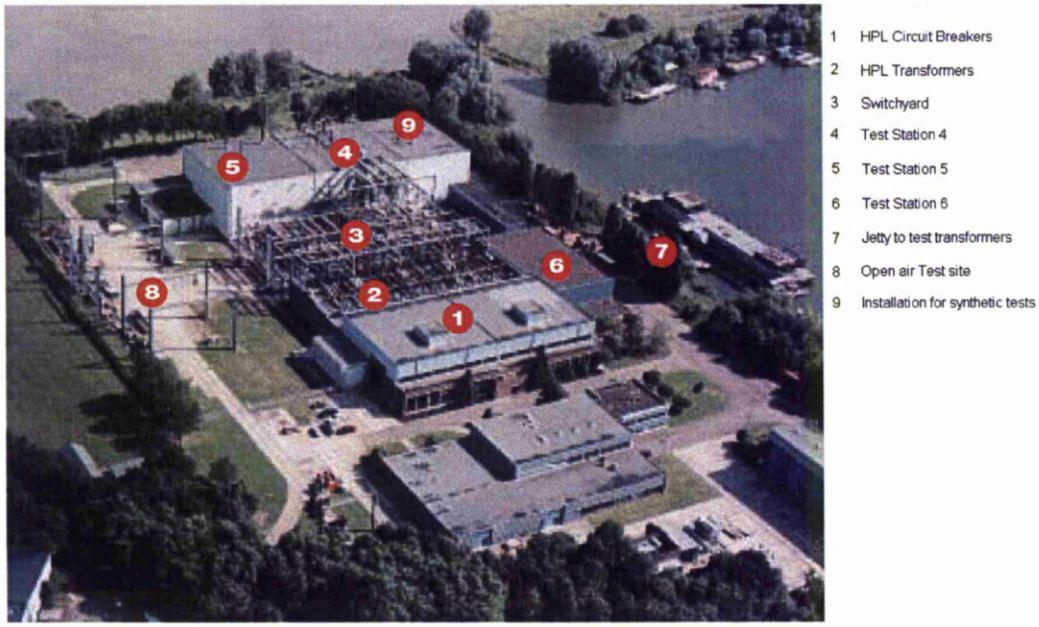


Figure 2-3: KEMA's High power test labs, *Kema* [2]

2.2 Sulphurhexaflouride

2.2.1 Introduction

Sulphurhexaflouride or SF_6 is used in the following applications:

- Insulation in high voltage applications
- Cover gas in Magnesium foundries
- Degasser in Aluminium casting
- Insulating gas in double glazing
- Plasma etching of Polysilicon and nitrite surfaces
- Atmospheric tracer for scientific studies
- Cushioning in soles of training shoes

SF_6 is a colourless, odourless, non-flammable and chemically stable inert gas. Stability comes from the symmetrical arrangement of the six fluorine atoms around the central sulphur atom and this stability is just what makes the gas useful in electric equipment. SF_6 gas has excellent insulating and arc-quenching properties and therefore has found a variety of applications in high voltage circuit breakers, *Maller & Naidu* [3]. There have been many attempts to find arc gas environments, which might compete with SF_6 as an efficient arc-extinguishing

medium. A range of pure gases and gas mixtures has been investigated, *Frind* [4] but a useful combination remains to be identified. This quest has recently been driven by the impetus fuelled by the realisation that SF_6 is one of the most potent greenhouse gases known, *Christophorou* [5]. However SF_6 is still used throughout the world in high voltage transmission networks and emissions arise during the manufacture and filling of electrical plant and from leakage and maintenance during the equipments lifetime. Pure SF_6 is not poisonous but it is an asphyxiant. It is not dangerous to inhale, provided that the oxygen ratio is high enough. In the UK the safe exposure limit is 1000 parts per million (ppm), *Air Liquide* [12]. SF_6 came into use approximately 50 years ago and since then some of the gas has leaked into the atmosphere. As the gas is very stable it will stay in the atmosphere for 4000 years and is 23,000 times more potent than CO_2.

2.2.2 The Greenhouse effect

Of the emissions into the atmosphere that are becoming of concern are: Greenhouse gases, air quality strategy pollutants, acidifying pollutant, Ozone precursors, base cations, persistent organic pollutants and heavy metals. Only the greenhouse gases and their effects are discussed here, however, information is readily available regarding the other emissions.

Thinning of the ozone layer means that more ultraviolet light can get to the ground; however, SF_6 unlike other gases does not destroy the ozone layer. The

gases that affect the ozone layer all contain chlorine and are broken up by ultraviolet radiation. This releaseds the chlorine that catalytically destroys ozone. The term "greenhouse effect" is commonly used to describe the notion that the atmosphere is slowly warming up due to man-made gas emissions. As well as SF_6 other gases that are contributing to the greenhouse effect are: carbon dioxide (CO_2), Methane (CH_4), Nitrous Oxide (N_2O), Hydrofluorocarbons (HFC) and Perfluorocarbons (PFC). These six greenhouse gases comprise the "basket of emissions", against which reduction targets were agreed at the third Conference of the Parties of the United Nations Framework Convention on Climate Change (UNFCCC) in Kyoto, Japan in December 1997. The target for the UK is to achieve a reduction of the global warming potential of the six greenhouse gases of 12.5 % by 2008-2012 (based on 1990 emission estimates), *Dore* [6]. However, in the 15th annual report from the UK National Atmospheric Emissions Inventory (NAEI) which is produced by the National Environmental Technology Centre, it has been found that the greenhouse gas SF_6 is the only pollutant showing an increase across the period 1970 to 2001, *Dore* [6]. The following table shows the global warming potential (GWPs) of UK greenhouse gas emissions which measures their effectiveness in global warming relative to CO_2, agreed by the intergovernmental panel on climate change (IPCC) for a 100 year time horizon.

Direct GHG	Emissions (ktonnes) in 2001	GWP (100 years)	Global Warming Equivalence (equivalent kT of CO_2)
CO_2 (as carbon)[1]	151,732	3.7	556,352
CH_4	2,195	21	46,105
N_2O	136	310	42,155
HFCs	2366	560-12100[2]	8,674
PFCs	192	6000-7400[2]	706
SF_6	522	23900	1,913

1. The emissions given here are on a UNECE basis and hence do not include land use change emissions.
2. A number of GWPs are used as this refers to a group of compounds.

Table 2-1: GWP for UK Emissions of Greenhouse Gases (2001), *Dore* [6]

CO_2 is biggest contributor to greenhouse gas emission in the UK and it comes mostly from the combustion of fossil fuels. Methane in the atmosphere is eventually oxidised to CO_2 and it is estimated that its lifetime in the atmosphere is about 12 years, *IPCC* [7]. Man-made (anthropogenic) Methane comes from waste disposal agriculture, Coal mining and leakage from the gas distribution system, *Dore* [6]. Nitrous Oxide (N_2O) emissions from the UK are low and the contribution is relatively small. HFCs and PFCs are industrial greenhouse gases like SF_6 and have high GWPs but compared to CO_2 the quantities emitted are very small.

Until the 1980s, there was very little direct evidence that temperatures worldwide were, in fact, rising. Against this background of uncertainty, even those politicians who were aware of the potential importance of this so-called

greenhouse effect for future generations adopted a policy of "wait and see". A key event which shifted the greenhouse debate towards the centre of the political stage was a conference on "The Changing Atmosphere", held in Toronto in 1988. A picture was presented to the delegates showing that average temperatures of the world would rise by up to 4°C over the next forty years, with sea levels rising by up to 140 cm, *Gribbin* [8].

With all of this taken into consideration it is therefore important that SF_6 is handled with great care, and that equipment is continually monitored for leaks and that SF_6 is recycled and or disposed of in a safe and reliable manner.

2.2.3 By-Products

SF_6 is a relatively non toxic gas, however, while it is inert during normal use, when discharges occur in SF_6, toxic by-products can be produced that can pose a threat to the health of workers that come into contact with them. SF_6 can decompose into by-products when exposed to four types of discharges *CIGRE* [9].

- Partial corona discharges caused by insulation defects;
- Spark discharges that occur at insulation defects or during switching operations;
- Switching arcs that occur in load break switches and power circuit breakers; and

- Failure arcs that occur due to insulation breakdown or switchgear interruption failure.

Numerous studies have characterised the by-products of SF_6. Dervos and Vassiliou (2000), Table 2-2, have summarised the most important ones (considering toxicity and risk) and the amounts of each formed under conditions similar to those found in SF_6 gas insulated switchgear equipment *ICF consulting* [10].

Chemical Formula	**Chemical Name**	**Chemical Abstracts Service Registry Number**	**Experimental Concentration (percent by volume)[a]**
HF	Hydrogen fluoride	7664-39-3	1.0
SOF_2 (SF_4)[b]	Thionyl sulphide (sulphur tetrafluoride)	7783-42-8 (7783-60-0)	0.5
SOF_4	Sulphur tetrafluoride oxide	13709-54-1	0.085
SiF_4	Silicon tetrafluoride	7783-61-1	0.085
S_2F_{10} (SF_5)[c]	Disulphur decafluoride	5714-22-7	0.025
SO_2F_2	Sulphuryl fluoride	2699-79-8	0.006
SO_2	Sulphur dioxide	7446-09-5	0.002

Table adapted from Dervos and Vassiliou (2000)

[a] Note that these concentrations represent the measured concentration for the experimental conditions studied. The conditions were designed to simulate a real sparking occurrence: however actual air concentrations in the vicinity of GIS will vary from these data.

[b] SF_4 is readily hydrolysed to SOF_2

[c] S_2F_{10} is referred to by some authors as sulphur pentafluoride or SF_5

Table 2-2: Gaseous SF_6 Decomposition by-products and typical concentrations during repeated sparking

There are other by-products that may be formed through these processes which include SF_2, SOF_{10}, $S_2O_2F_{10}$ and H_2S as well as a number of metal fluorides, aluminium fluoride and tungsten compounds *ICF Consulting* [10].

Governments provide web pages and information regarding hazardous substances. In the UK, the Health and Safety Commission (HSC) and the Health and Safety Executive (HSE) are responsible for the regulation of almost all the risks to health and safety arising from work activity in Britain. Exposure limit tables are produced under the control of substances hazardous to health (COSHH) and data on substances are readily available. By-products of SF_6 such as SF_4, SiF_4, SO_2F_2, SO_2 and HF are extremely irritating to the eyes, nose and throat *NLM* [11]. Other effects of these gases include pulmonary edema, skin and eye burns, nasal congestion, and bronchitis due to their corrosive characteristics. There have also been animal tests that indicate these bi-products are extremely irritating when inhaled. Animals exposed to these gases via inhalation exhibit lung damage (e.g., lung irritation, edema, and hemorrhages) *ICF Consulting* [10]. There have been several incidents reported regarding exposure to by-products of SF_6 and these can be seen listed in the report prepared by ICF contained in the appendices. Also contained in this report are exposure limits for solid and gaseous by-products. Therefore it can be seen that great care must be taken when handling SF_6. Appendix III contains a document outlining SF_6 handling procedures for the University of Liverpool.

2.3 The Mass Spectrometer

2.3.1 Introduction

Gas Chromatography is a method of separating and identifying the components of a gas mixture. The coupling of gas chromatography with mass spectrometry is probably the oldest hybrid technique in instrumental analysis *Hübschmann* [13]. The number of articles which were written on each individual technical aspect during the development of the method is enormous and there are many articles on its applications. There are other methods of gas analysis including non-dispersive infra-red gas analysis, *Powell* [14]. Mass spectrometry is a technique used to obtain information about an analyte so as to characterise the analyte's molecular weight and sometimes infer structure. The first functioning of the mass spectrograph was built by *Aston* [15] in 1919 to support his work in the discovery of stable isotopes of some elements for which he won the Nobel Prize in chemistry in 1922. During this period, A. J. Dempster developed an area of positive-ray analysis called abundance spectrometry, *Dempster* [16], which evolved into modern mass spectrometry, *Watson* [17]. The mass spectrometer works by transferring some energy to a sample so that it becomes ionised. The ionised sample is then separated according to its mass to charge ratio m/z. In classical mass spectrometry a bar graph mass spectrum is then produced which gives abundances at each molecular weight and is usually measured in atomic

mass units (AMU). The term mass spectrometry can be deceiving as samples are separated according to their mass to charge ratio rather than there mass alone.

2.3.2 Different types

The four most common types of mass spectrometer are magnetic sector, Quadrupole, Ion trap and time of flight. The instrument used in this project is a Residual Gas Analyser or RGA, which is a type of Quadrupole and will be discussed in detail in further sections. A basic review of the other three types of mass spectrometer is given.

2.3.2.1 Magnetic Sector

The magnetic sector uses a wedge shaped magnetic field to separate the total ion beam from the ion source into discrete ion beams of individual m/z values through momentum dispersion and direction focusing, *Trainor* [18], Figure 2-4. However the Magnetic sector mass spectrometer is very expensive and requires skilled operators.

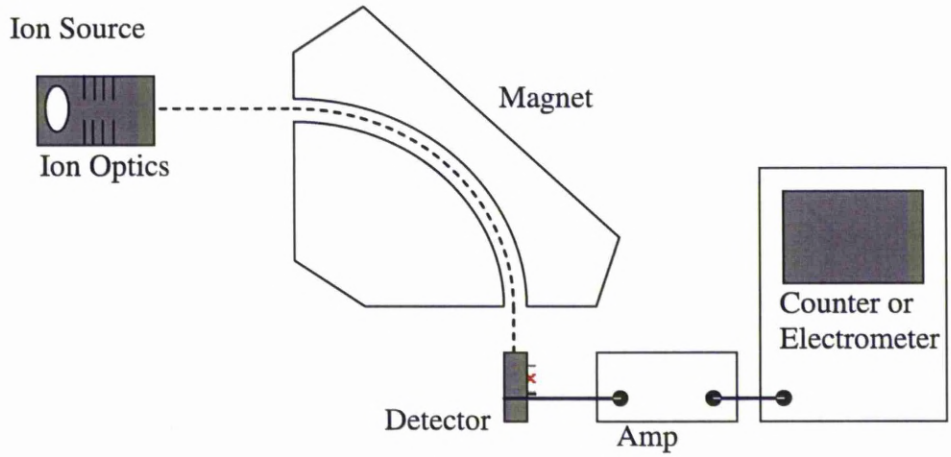


Figure 2-4: Magnetic Sector

2.3.2.2 Ion Trap

The ion-trap mass spectrometer uses three electrodes to trap ions in a small volume, Figure 2-5.

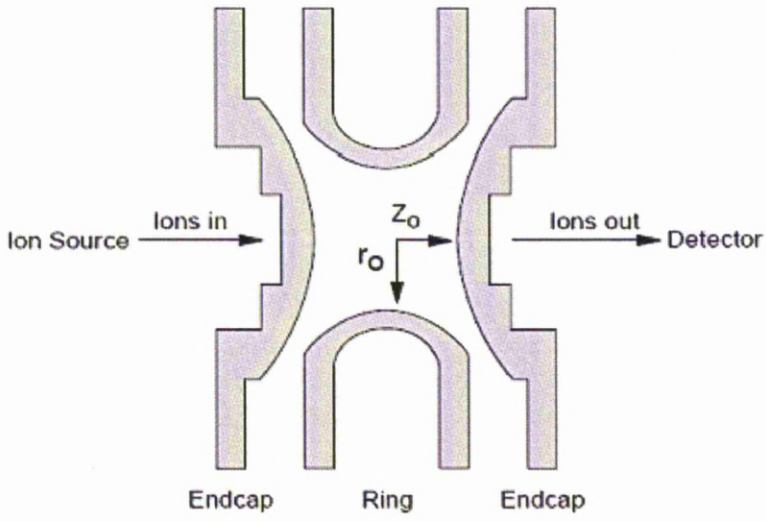


Figure 2-5: The Ion trap, *Wong* [19]

The ion trap consists of a ring electrode and two hyperbolic endcap electrodes. The motion of the ions induced by the electric field on these electrodes traps ions. The radio frequency is scanned to excite and eject ions through small holes in the endcap to a detector. At higher RF frequencies, higher m/z ions are excited. The different RF frequencies are produced by changing the electrode voltages. The ion trap mass spectrometer is similar to the quadrupole which will be explained in detail. The difference is that with the ion trap, the ions are trapped in three-dimensional space, whereas in the quadrupole mass filter they are confined only in two-dimensional space, *Watson* [17].

2.3.2.3 Time of flight

A time-of-flight (TOF) analyser is one of the simplest mass analysing devices.

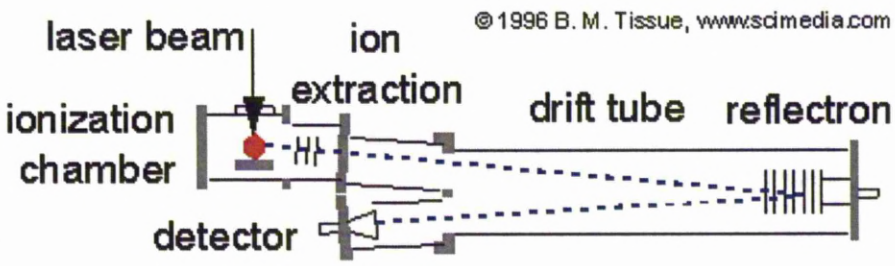


Figure 2-6: Time of Flight Mass Spectrometer, *Tissue* [20]

Time-of-flight analysis is based on accelerating a set of ions to a detector with the same amount of energy. Figure 2-6 shows ablation of ions from a solid sample with a pulsed laser. The reflectron is a series of rings or grids that act as an ion mirror. This mirror compensates for the spread in kinetic energies of the ions as they enter the drift region and improves the resolution of the instrument. The output of an ion detector is displayed on an oscilloscope as a function of time to produce the mass spectrum. Because the ions have the same energy, yet a different mass, the ions reach the detector at different times. The smaller ions reach the detector first because of they have a greater velocity and the larger ions arrive later.

2.3.3 Residual gas analyser

A residual gas analyser (RGA) is a small mass spectrometer that can be connected directly to a vacuum system. Gas molecules/atoms are ionised (usually positive ions) and are separated, detected and measured according to their molecular/atomic mass. This thesis contains experiments carried out on two instruments the first of which is manufactured by Stanford research systems model number RGA300 and consists of a quadrupole probe and associated circuitry, and is used with an external vacuum system, Figure 2-7 shows the quadrupole probe.

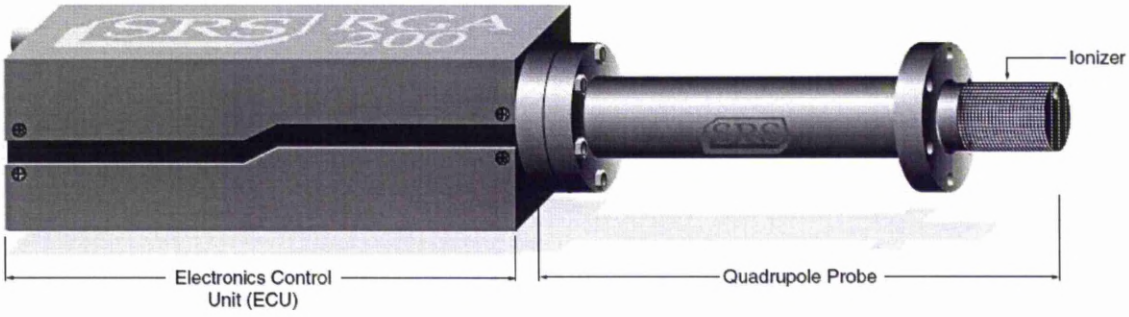


Figure 2-7: Residual Gas Analyser, *Stanford Research Systems* [21]

The second instrument is a CIRRUS (LM99) manufactured by MKS Instruments and consists also of a quadrupole probe, associated circuitry and an integrated vacuum system, Figure 2-8.

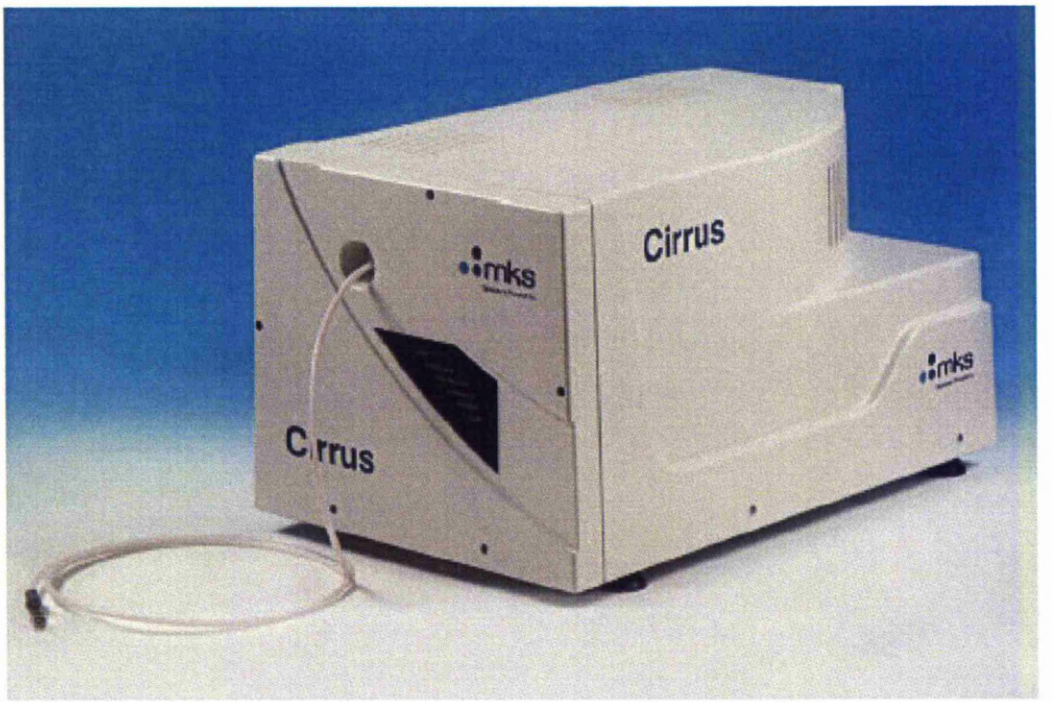


Figure 2-8: Cirrus (LM99), *MKS* [22]

The basic quadrupole mass spectrometer consists of an ioniser, a quadrupole filter and an ion detector, Figure 2-9. However a vacuum system and associated software and circuitry are also needed for obtaining mass spectra.

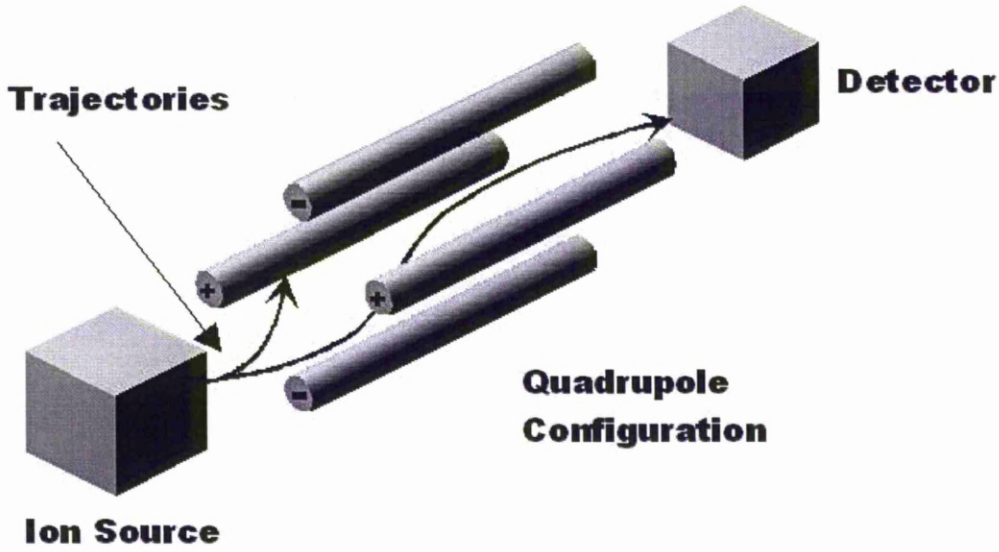


Figure 2-9: Quadrupole mass spectrometer

2.3.3.1 The Ioniser

An ion is created when a neutral atom/molecule gains or losses an electron. An RGA is described as a positive ion mass spectrometer when atoms/molecules lose electrons. Conversely, when the atoms/molecules gain an electron it is referred to as a negative ion mass spectrometer. When an atom gains or loses electrons, it changes its charge.

An electron is lost when a beam of electrons is targeted at the atoms/molecules, which may subsequently remove an electron from them. For example, a sodium atom can lose an electron in the following equation:

$$Na + 1 \text{ (fast) electron} \rightarrow Na^{+} + 2e^{-} \qquad 2\text{-}1$$

Once electron transfer has occurred, the atom/molecule is then referred to as an ion (atomic ion or molecular ion). Atoms/molecules can only be neutral and ions can only be charged. The RGA uses a filament to provide an ionising electron beam.

The ionisation energy (IE) is the amount of energy required to remove one electron from an atom. Thus, it measures how strong the outermost electron is attached to the atom. Some atoms have more than one IE. When this is the case, the IE energies are referred to as the "first ionisation energy" or 'I', "second ionisation energy" or 'I_2', and so on. Note that the energy variable convention follows I_i where "i" is the orbital from which the electron is lost. Ionisation is endothermic (takes energy from an outside source) meaning that the atom or molecule increases its internal energy. The equation for the first ionisation energy is shown above, the equation for the second ionisation energy is:

$$Na^+ + e^- \rightarrow Na^{2+} + 2e^- \qquad 2\text{-}2$$

In general, the smaller the atom the closer the valence electrons are to the nucleus. This means the attractive force holding the electron is stronger and therefore it takes more energy to remove additional electrons. The ionisation energy values can be found in myriad chemistry books. A plot of first ionisation energy against atomic number can be seen below in Figure 2-10:

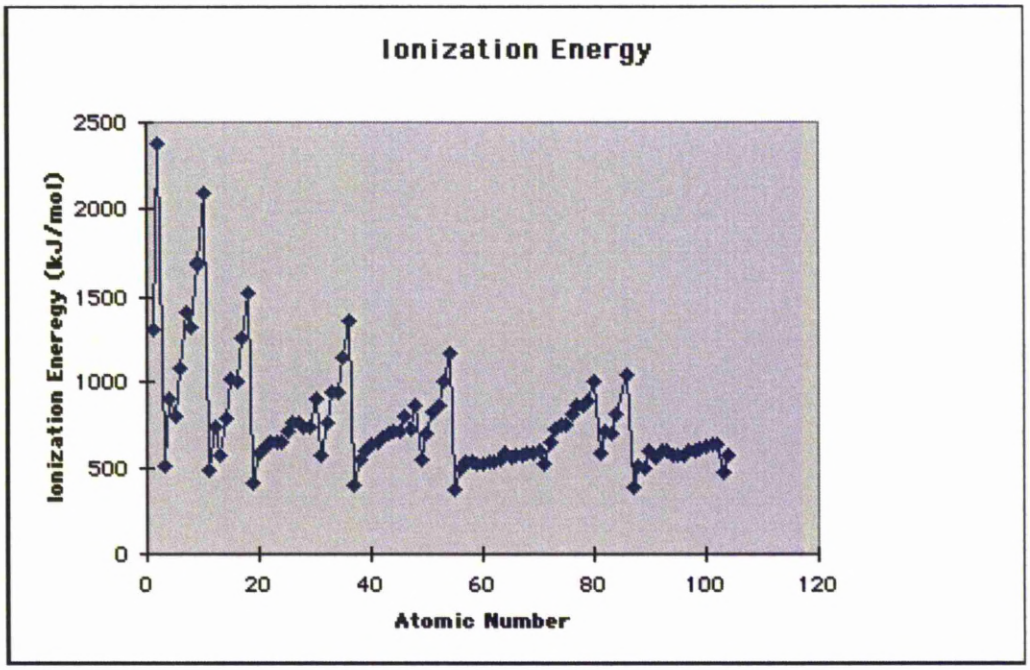


Figure 2-10: Ionisation Energies in kJ/mol, *Shodar* [23]

It can be seen in the above figure that the IE overall diminishes with atomic number. As you increase atomic number, there are more electrons and more shells to accommodate them. They get progressively further away from the nucleus so the positive charge has less of a hold on them so the IE decreases. The IE refers to the first electron in the outermost shell, so the outermost shell is getting further away from the nucleus. When an outermost shell has only one electron in it then only a relatively low IE is required to remove it. When there are 2 electrons then the energy is a bit higher. This continues until the shell is full where the ionisation energy reaches a peak and then falls due to another shell

starting (containing 1 electron). This can be seen in the form of peaks and troughs in the figure above

The SF_6 molecule consists of 1 Sulphur atom and 6 Fluorine atoms, Figure 2-11. The total mass of a SF_6 molecule is the sum of the Sulphur (approximately 32 AMU) and 6 Fluoride (approximately 19 AMU per fluoride):

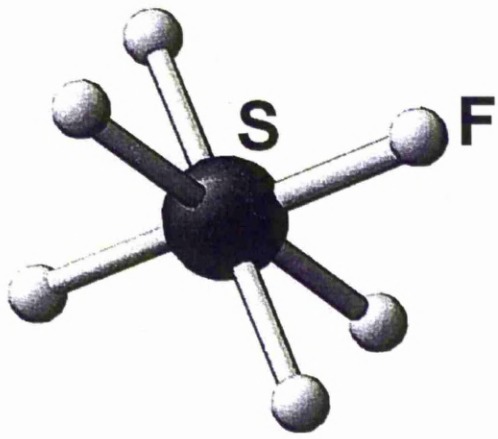


Figure 2-11: The SF6 molecule

Therefore the total mass of SF_6 is: $32 + (6 \times 19) = 146$ AMU. If an electron beam is targeted at the SF_6 molecule as is in the ionisation process for the mass spectrometer, it may be expected based on the previous simple explanation that SF_6^+ will be produced. However, the electrons hit the molecule such that the SF_6 disassociates into smaller fragments i.e. SF_5^+, SF_4^+, SF_3^+, SF_2^+, SF^+, S^+ and F^+. The SF_6 does not stay intact and only the fragmented ions are detected. There may however, already be some SF_5 in the air since the arcing process in circuit

breakers may disassociate SF_6 and this would be a good indication of SF_6 presence, however as will be seen in chapter 4 this will not affect results since we will be looking at the SF_5^+ peak which is not affected. From Figure 2-10 the ionisation energy to remove an electron from a Fluorine molecule is 1680 kJ/molecule = 17.412 eV and for Sulphur the energy is 999.6 kJ/molecule = 10.36 eV. However, as SF_6 is a molecule, calculation of the ionisation energy becomes more complicated and will not be discussed here. Experiments have been performed in the past to determine the ionisation energy for SF_6 and details can be found on the national institute of standards and technology (NIST) web-book online. The value was calculated to be between 15.30 eV – 15.70 eV, *NIST* [24].

In a residual gas analyser a filament provides ionisation. The ioniser settings can be directly controlled and monitored. Table 2-3, taken from the instructions of the RGA300 summarises the ioniser settings available to the user, including default factory values, parameter ranges and minimum acceptable increments:

	Units	**Default**	**Range**	**Min. Incr.**
Ion Energy	eV	12	8 (low) or 12(high)	n.a.
Electron Energy	eV	70	25 to 105	1
Focus Voltage	V	-90	0 to –150	1
Emission Current	mA	1.00	0 to 3.5	0.02

Table 2-3: Ioniser Settings, *Stanford Research Systems* [21]

The ion energy is the kinetic energy of ions as they move down the ion filter and is equal to the voltage biasing of the anode grid. The ion setting affects the sensitivity of the spectrometer i.e. the magnitude of the signals collected. The resolution is also affected. The electron energy is equal to the voltage difference between the filament and the anode grid. For electrons to produce ionisation of gas molecules by bombardment, they must have a certain minimum kinetic energy. This minimum is different for every molecule. Above this minimum the ionisation efficiency increases until a maximum is reached and the maximum is usually in the range of 50eV –100eV.

2.3.3.2 Quadrupole Filter

The theory of the quadrupole is based on the following equation which gives a three dimensional electric field described by the potential variation:

$$\phi(x, y, z) = \phi_0 \frac{(x^2 - y^2)}{2r_0^2} \qquad \textbf{2-3}$$

This equation is invariant along the z axis and the potential distribution satisfies the Laplace equation. For a particular value of ϕ_0, the equipotentials in the xy plane are four rectangular hyperbolas with asymptotes at 45° to the Cartesian axis, indicated in the Figure 2-12, *Batey* [25].

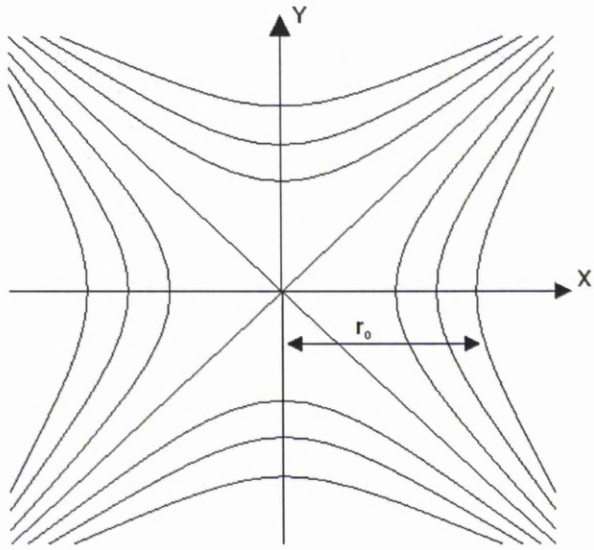


Figure 2-12: Quadrupole Field

The quadrupole mass filter is what determines which ions reach the detector at any given time. It is operated by a combination of radio frequency (RF) and DC voltages and the filtering action is dependant on the ion trajectories. The magnitude and frequency of the RF determine the mass-to-charge ratio of the ions that can pass through the filter without striking the rods. The frequency of operation of the quadrupole in the RGA300 is 2.7648 MHz. The CIRRUS has a triple filter quad (pre and post, RF only filters) with a closed ion source and multi channel plate electron multiplier (see section on electron multipliers). This quadrupole runs at 1.8432 MHz and uses a quartz crystal. The quadrupole and filament, must be operated in a vacuum of no more than 10^{-4} Torr. The mass range of the quadrupole (lightest and heaviest singly charged ions) is dependant on the

supply voltage available to the rods. The manufacturers of the RGA300 offer three models giving 1 to 100 AMU, 200 AMU or 300 AMU measurement capabilities. The CIRRUS has a range 1 to 300 AMU. The resolution of the RGA300 is factory set to 1 AMU; however, the RGA has two available ion energy settings, which correspond to ultimate resolution values of approximately 0.3 AMU (8eV) and 0.5 AMU (12eV), *MKS* [22]. The CIRRUS has an advantage as the resolution can be tuned under calibration conditions.

2.3.3.3 Resolution

The resolution is the resolving power and is a measure of the peak width and it is normally set so that when the peak is at 5% of the peak height then the width is 1 AMU, Figure 2-13.

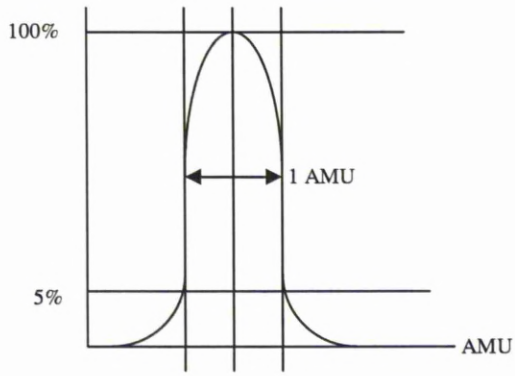


Figure 2-13: Resolution

The resolution is important when trying to decipher individual partial pressure peaks that are close together. However, when looking at an isolated

partial pressure peak the resolution is not as critical and the signal can be improved by reducing the resolution.

2.3.3.4 Detector

The detector in a residual gas analyser is either a Faraday cup or an electron multiplier and measures the ion currents.

Faraday Cup

The principle of operation for the Faraday cup, Figure 2-14, is that a change in charge on a metal plate produces a flow of electrons, which can be measured as a current. Ions strike the dynode surface of the Faraday cup, which then emits electrons and induces a current, which is recorded using a sensitive electrometer. Currents measured are of the order 1 x 10^{-9} to 1 x 10^{-15} Amps for pressures in the range 10^{-5} to 10^{-11} Torr, *MKS* [22].

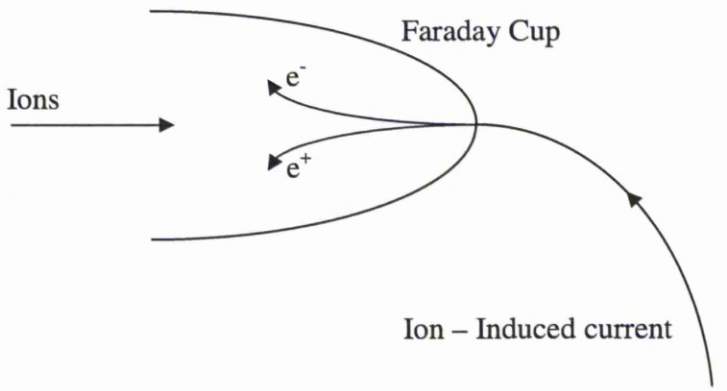


Figure 2-14: Faraday Cup

However, in real time applications, Faraday cup detectors are rarely used to measure partial pressures below 10^{-9} Torr. At pressures below that, there is an option of using an electron multiplier, which allows for faster scan rates and improved signal to noise ratios. The CIRRUS has the option of switching between faraday cup and electron multiplier whereas the RGA300 does not have an electron multiplier. The CIRRUS electron multiplier has a ×100 or ×20k option for more sensitivity.

Electron Multiplier

An electron multiplier measures an ion signal proportional to the ion current. The basic physical process that allows an electron multiplier to operate is called secondary electron emission. When a charged particle, neutral particle, an ion or an electron strikes a surface, it can liberate electrons associated with the outer layers of atoms. The number of secondary electrons released depends on the type of incident primary particle, its angle, energy and characteristics of the incident surface. In general there are three basic forms of electron multipliers that are commonly used in mass spectrometry; the discrete-dynode electron multiplier, the continuous-dynode electron multiplier and the microchannel plate. Whereas a Faraday cup uses one dynode, the discrete dynode electron multiplier is made up of a series of dynodes maintained at ever increasing potentials. Ions strike the dynode surface, resulting in the emission of electrons. These secondary electrons are then attracted to the next dynode where more secondary electrons are

generated, ultimately resulting in a cascade of electrons. Typical amplification or current gain of an electron multiplier is one million, see Figure 2-15

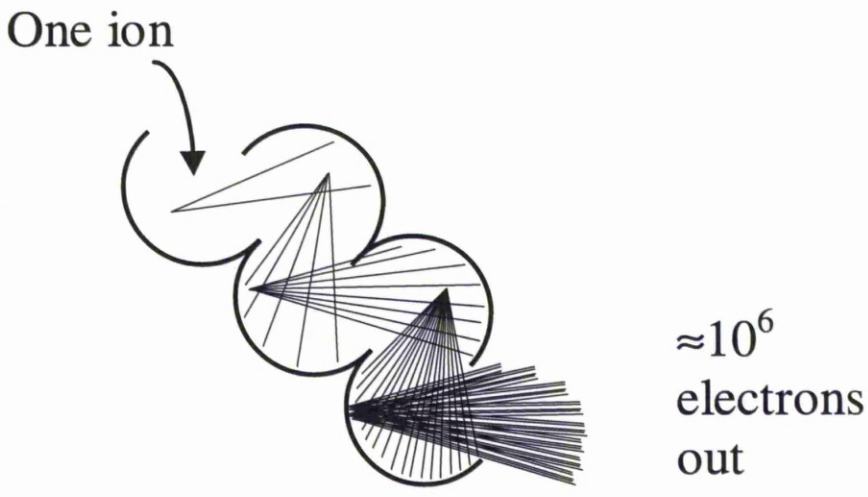


Figure 2-15 Discrete dynode Electron Multiplier

The resulting electron current is proportional to the ion current and is measured in the same manner. For the continuous channel electron multiplier (CEM) the amplification is provided by a continuous surface made from a special glass, Figure 2-16. The inner surface is conductive, typically with a resistance of 80 – 100 MΩ. The process of charge amplification is similar to that which occurs in a discrete dynode multiplier, except that the process is distributed along the

length of the channel. The main advantages of the CEM are its small size and its tolerance for exposure to ambient air, *Batey* [25].

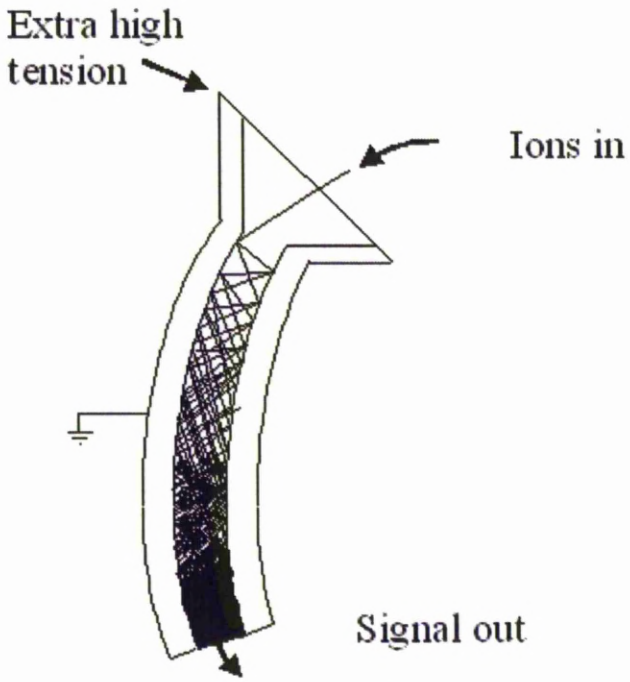


Figure 2-16: Continuous channel electron multiplier

The electron multiplier in the CIRRUS is a microchannel plate. This multiplier operates much the same as the CEM but there are many channels rather than one spread out uniformly, Figure 2-17. The gain is limited to 10^5, although it is possible to cascade the devices, *Batey* [25]. This device is used as a low cost alternative to CEM and the glass used is usually of a much higher resistance than the CEMs.

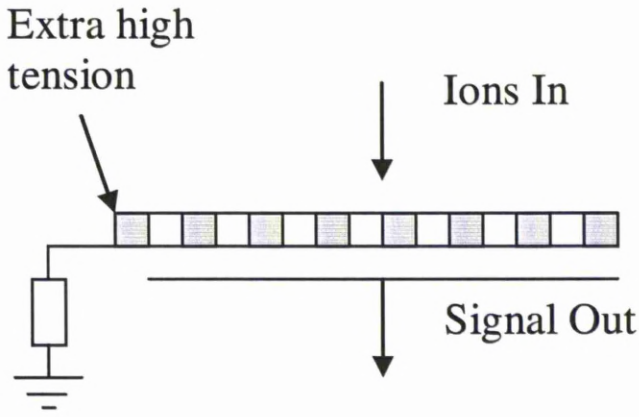


Figure 2-17: Micro Channel plate

The sensitivity of the spectrometer increases with the gain of the multiplier. However, the increase in sensitivity gives rise to limited dynamic range, mass discrimination effect, gain instabilities and finite lifetime of the device, *Stanford Research Systems* [21]:

- Dynamic range: This is determined by its dark current at the low end and the bias current at the high end.
- Mass discrimination: As the size of the ions increases then the gain decreases due to the ion-electron conversion efficiencies on the velocities of the ions entering the detector.

- Gain instabilities: As time goes by the gain of the multiplier changes unavoidably. Therefore, frequent calibration is required with the Faraday cup.
- Finite Lifetime: As the gain changes with time, eventually it drops to unacceptable levels and the multiplier needs replacing.

2.3.4 Software Packages

The flexibility of a residual gas analyser depends on among other things the software package which controls it. The RGA300 RGA uses a package written by Stanford Research Systems and is simply called SRS RGA Version 2.3. It was written in 1996 and is DOS based and quite limited. There are just 7 modes of operation: Analogue, Histogram, Table, Pressure verses Time, leak test, annuciator and Library mode. This project uses only analogue mode which can scan anywhere between 1 to 300 AMU. The CIRRUS uses a software interface called Process Eye Professional version 4.03 developed by MKS instruments. The Process Eye Professional package is designed to monitor partial pressures and optionally, analogue and digital inputs. The data acquisition is fast and covers a wide dynamic range of pressures so that some, or all of the partial pressures, along with analogue and digital inputs, can be measured and stored, while only data of interest is displayed. The package has been designed to be configured by the

process engineer, who can set up a number of pre-set configurations called "recipes" for various production requirements. These can then be selected by an operator with a single click on a named button, *MKS* [22].

2.4 Gas dispersion models

2.4.1 Introduction

This project is concerned with measurement of gas leaking from switchgear, therefore, it is important that the movement of gas is understood. This section will explore various models that can be used to estimate how SF_6 will behave after leaking from a system into ambient air.

Modelling is an essential tool in Engineering and can be divided into two types:

- Physical models, small-scale laboratory experiments (e.g. wind tunnels etc.)
- Mathematical models, which are a set of mathematical algorithms that can describe the problem.

Chapter 4 discusses the application of a physical model and describes the construction and testing performed on such a model. This section is concerned with a review of some mathematical models.

2.4.2 The different models

It is useful to derive a simple model of a leak to simulate the dispersion of gas from a leak in the laboratory. Similar models have been used in the smoke stack industry to estimate air pollution over large scales. There are three main types of air pollution models; they are Gaussian, Eulerian and Lagrangian. A brief description of each model is given:

2.4.2.1 The Eulerian and Lagrangian model

The Eulerian model is used to track a single cloud of one substance as it travels through another substance with respect to time. The equation looks at pollution as it travels through air, but of course the model can also be used to track particles entering a liquid for example, *Holbeach* [27]. The Eulerian model is based on the fact that a substance will collide with another substance that surrounds it, resulting in a different shape, size and diffusion. The Lagrangian model provides an alternative to the Eulerian and is so called because it describes the fluid elements that follow the instantaneous flow, *Zannetti* [28].

The difference between the Lagrangian and Eulerian models is that the Eulerian model is referenced to the ground whereas the Lagrangian model is referenced to the pollutant (average atmospheric motion), Figure 2-18.

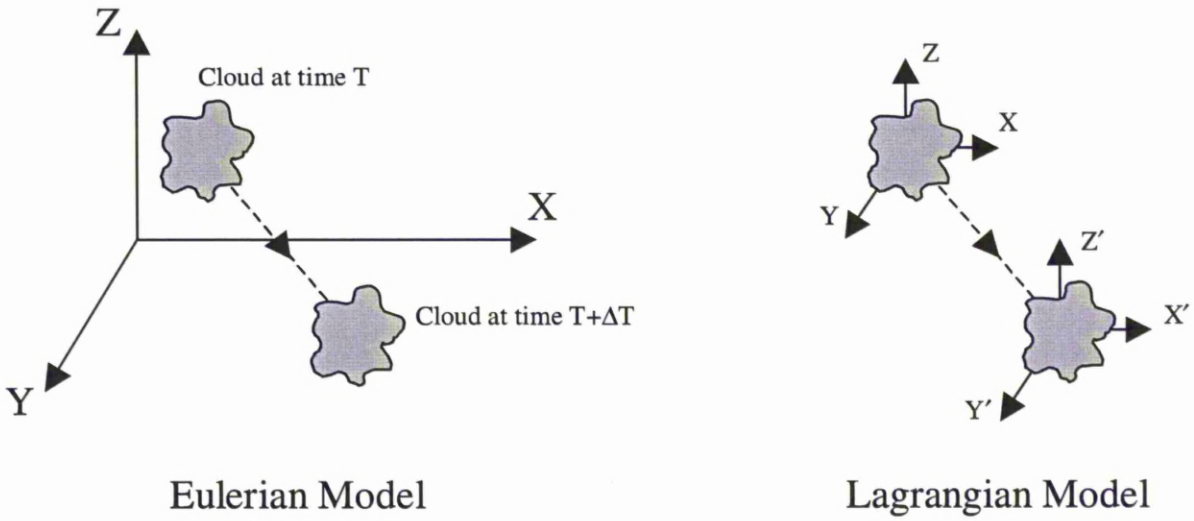


Figure 2-18: Eulerian and Lagrangian models

There is a lot of information that can be found regarding the two models and they are commonly used to assess pollution etc. over large areas such as city's and countries. However the equations are complex and have lots of variables; therefore they shall not be studied in depth.

2.4.2.2 The Gaussian model

The Gaussian model is the simplest of the three and is therefore the most commonly used. In general the Gaussian formula is represented by:

$$C(x,y,z)=\frac{Q}{2\pi\sigma_y\sigma_z\bar{u}}e^{-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2}e^{-\frac{1}{2}\left(\frac{h-z}{\sigma_z}\right)^2} \qquad \textbf{2-4}$$

Where

- C is the pollutant concentration (g/m^3)
- x, y, z is the distance from the point of origin in x, y, z co-ordinates (m)
- Q is the pollutant source emission rate (g/s)
- σ_y is the standard deviation of the horizontal turbulence distribution (m)
- σ_z is the standard deviation of the vertical turbulence distribution (m)
- h is the effective height of the pollutant (m)
- $\bar{u}$ is a the average horizontal wind speed at the pollutant height (m/s)

The equation is not overly complicated except for the two terms σ_y and σ_z. As explained above, these two terms represent the standard deviation of the turbulence and is dependant on the distance x. It is assumed that the atmosphere is stable and therefore, *Barratt* [29],

$$\sigma_y = 0.067x^{0.90} \quad \text{and } \sigma_z = 0.057x^{0.80} \qquad 2\text{-}5$$

This equation assumes that the wind speed is constant in the direction of x, however, if the model is for a circuit breaker indoors then there is no wind speed meaning that this model cannot be used. Also, since the 3 measurement points are on 1 plane, height can be ignored. Therefore, in laboratory conditions it is

assumed that a point source gas will spread out as a Gaussian distribution and a diffusion coefficient is incorporated, Figure 2-19.

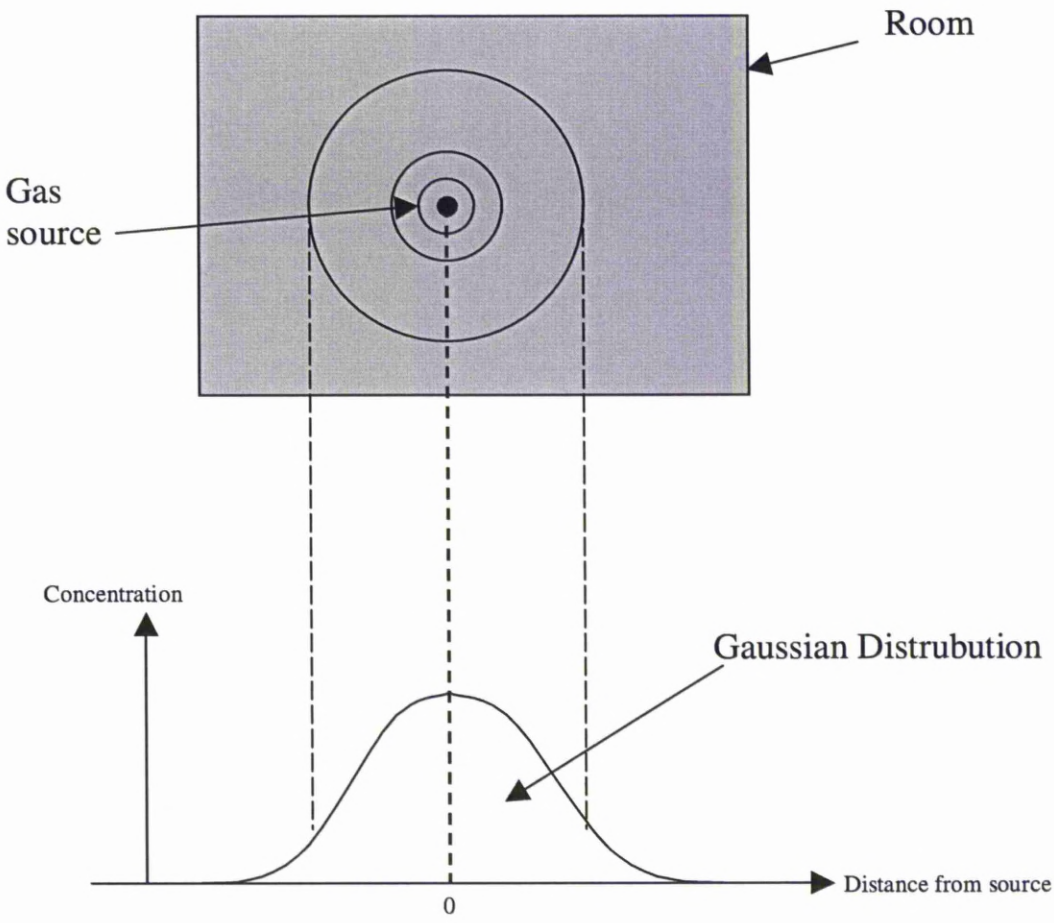


Figure 2-19: Gaussian distribution

Assuming this Gaussian distribution then a minimum of three detectors is all that is needed to determine the position and strength of the source, Figure 2-20.

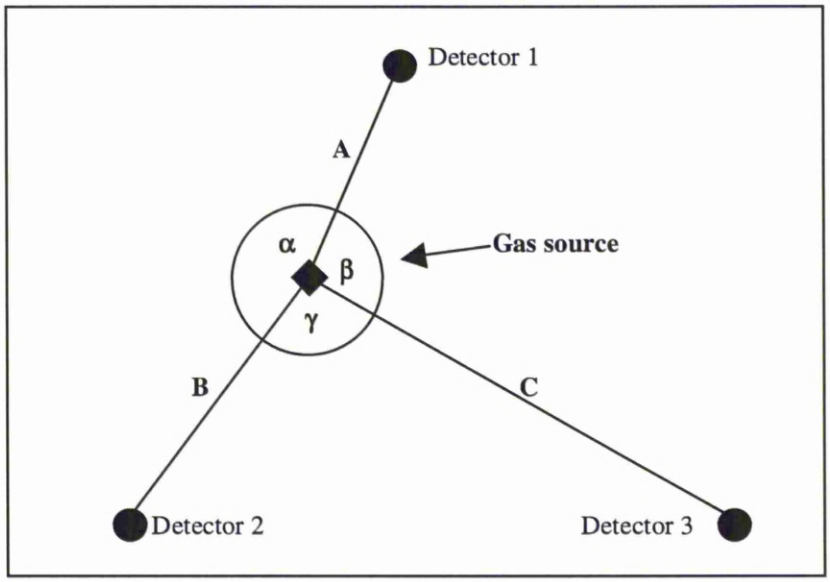


Figure 2-20: Three-point measurement system

The strength of the signal at each detector will be directly proportional to the distance from each detector to the source regardless of the flow rate of the leak. If there is no wind speed or height (lab conditions) and the gas dispersion has a normal distribution, the equation to determine source concentration is:

$$C = Qe^{-\frac{1}{2}\left(\frac{r^2}{d^2}\right)} \qquad \textbf{2-6}$$

C = Concentration at a point of distance r

Q = Source Concentration

d = Dispersion coefficient

r = Distance from the source

In the above equations concentrations in air are measured in units of the mass of chemical per volume of air (mg/m^3). However, in this project concentrations are expressed parts per million (ppm) or parts per billion (ppb). For SF_6 (molecular weight of approximately 146) in air it is assumed that there is a pressure of 1 atmosphere (7.6×10^2 mm Hg) and a temperature of 25° C. Under these conditions, the equation to convert from concentration in PPM to concentration mg/m^3 is *SMARTE* [30]:

$$C(mg/m^3) = \frac{C(ppm) \times 146}{24.45} \qquad \textbf{2-7}$$

The number 24.45 is the volume in litres of a mole of gas at 1 atmosphere and 25° C. However, if the temperature or pressure changes then the following equation must be used:

$$C(mg/m^3) = \frac{P \times C(ppm) \times 146}{62.4 \times (273 + T)} \qquad \textbf{2-8}$$

T = Temperature (Celcuis)

P = Pressure (Torr)

2.5 Chromatic monitoring

2.5.1 Background

Optical measurement is used throughout industry due to its many benefits such as it can be used in environments such as explosive, high temperature etc.. It can also be used in other areas where there may be high magnetic or electric fields which would make normal electronic systems inadequate. Also, light is non intrusive and can be used to monitor systems without affecting their function. In the past optical sensors have been seen to be expensive or insufficiently robust to withstand the industrial environment *Jones* [31]. However the methodology is developing all the time and sensor companies are now providing fibres that are much tougher, Figure 2-21. The latest fibres can now withstand higher temperatures and are much more flexible etc.

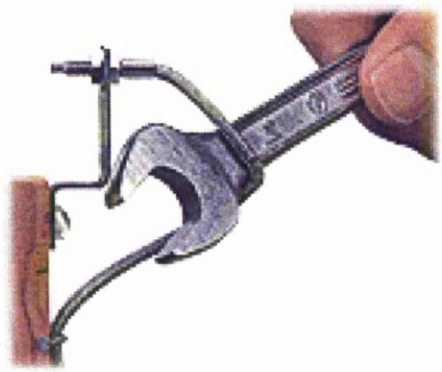


Figure 2-21: Tough Fibre Optic currently on the Market, *Keyence* [32]

2.5.2 Introduction

A technique has been developed called chromatic monitoring which offers the possibility of using existing sensors which overcomes many of the difficulties which are inherent in spectral or two-wavelength monitoring methods that are traditionally used in optical measurement.

This section aims to discuss the concepts of chromatic monitoring. The chromatic parameters hue, lightness and saturation (H, L, and S) will also be explained. It is also described how these concepts taken from the optical domain can be transferred and used in different domains, such as acoustic, temperature and in this project, atomic mass units and space. A chromatic technique is also explained which has the potential for identifying emergent patterns from mass spectra.

The word chromatic comes from the Greek word "chromatikos", which means coloured. All colours other than the neutral colours white, black, and the pure greys, are chromatic. Therefore, chromatic monitoring is a means to quantify colour. However, this is an oversimplification of the full capabilities of the method. There have been a number of applications of chromatic monitoring including plasma monitoring *Jones* [33], Wavedriver battery fault analysis *Hon Lu Li* [34], Transformer failure monitoring, *Zhang Jinghua* [35] and many more. To obtain information about colour, light emitting diodes (LED's) are used in

conjunction with optical or photo sensing detectors and a transmission medium such as air or optical fibres. When performing a chromatic inspection of light the wavelength and intensity are used. The chromatic process involves the derivations of the lights' hue, saturation and lightness. Therefore, the complex detailed spectral signature of the light signal has been reduced to 3 simple values which represent the signal. To understand this, the concept of colour is discussed.

2.5.3 Colour

Light is a form of radiant energy or energy that travels in waves. Usually when light is discussed it is only the radiation that the human eye can see which is referred to. These wavelengths range from approximately 400 to 700 nm. There are other forms of light radiation that the human eye cannot see such as ultraviolet light (lower than 400 nm) and infra red light (higher than 700 nm). The first explanation of colour was provided by Sir Isaac Newton in 1666. Newton passed a beam of sunlight through a prism and showed that it bent or refracted to produce a spectrum. He also proved that different colours are bent through different angles, Figure 2-22.

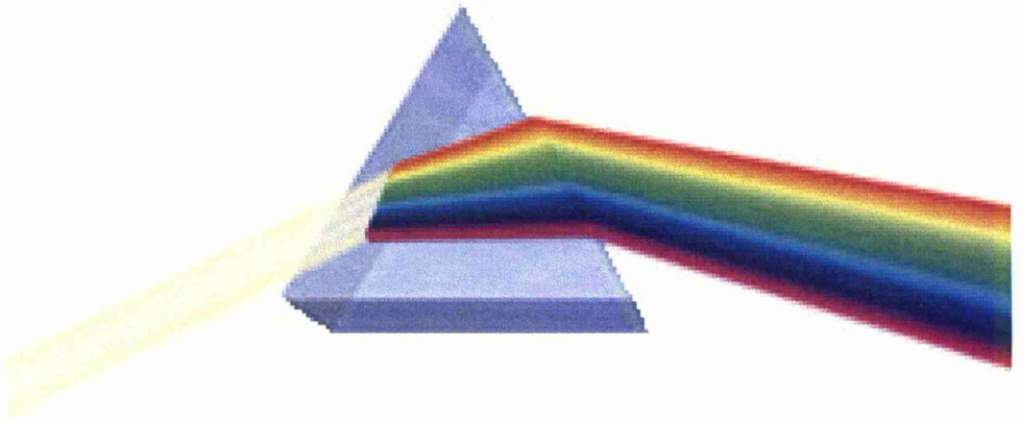


Figure 2-22: Newton's 1666 prism experiment

Since different colours have different wavelengths this means that they will travel at different speeds through the prism and that is why the light separates i.e. red has a long wavelength and will propagate through the prism quicker than blue light, which has a shorter wavelength. The human eye picks out sections of the visible spectrum and assigns each section to one colour; these colours are commonly known as red, orange, yellow, green, blue, indigo and violet. The retina of the eye is equipped with two types of receptor, "rods", which are sensitive only to average light intensity and the cones, of which there are three types, each type being sensitive to a different wavelength, *Dean* [36]. The eye discriminates colour via the relative light intensity received by each type of retinal cone. Figure 2-23 illustrates the principle of colour mixing. The red, green and

blue circle can be considered as the three different types of retinal cone, having responses in the centre of each circle. Therefore, if the cones each receive and equal amount of energy then the colour that is perceived is white. Hence if the red and green cones receive an equal amount of energy and the blue receives none, then the colour that is perceived is yellow etc. This perceived shade of colour is known as the "hue".

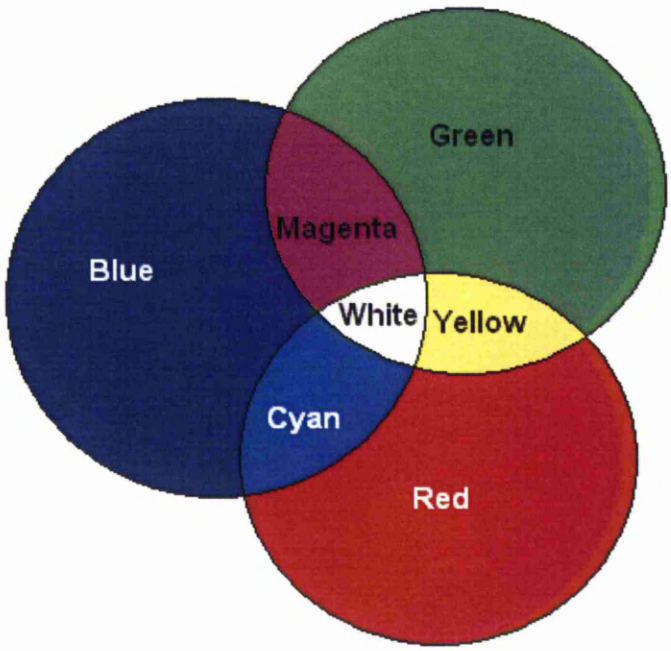


Figure 2-23: Additive Colour mixing

The perceived colour is also dependant on two other factors, the "saturation" and the intensity, or "lightness", *Dean* [36].

2.5.4 Quantitative measurement

In the earlier part of the 20th century experiments enabled the response of the eye to be characterised and Figure 2-24 shows the three CIE (The Commission Internationale de L'Eclairage) colour matching functions (CMF's) *Steer* [37]. These responses are closely mathematically related to the responses of the human eye.

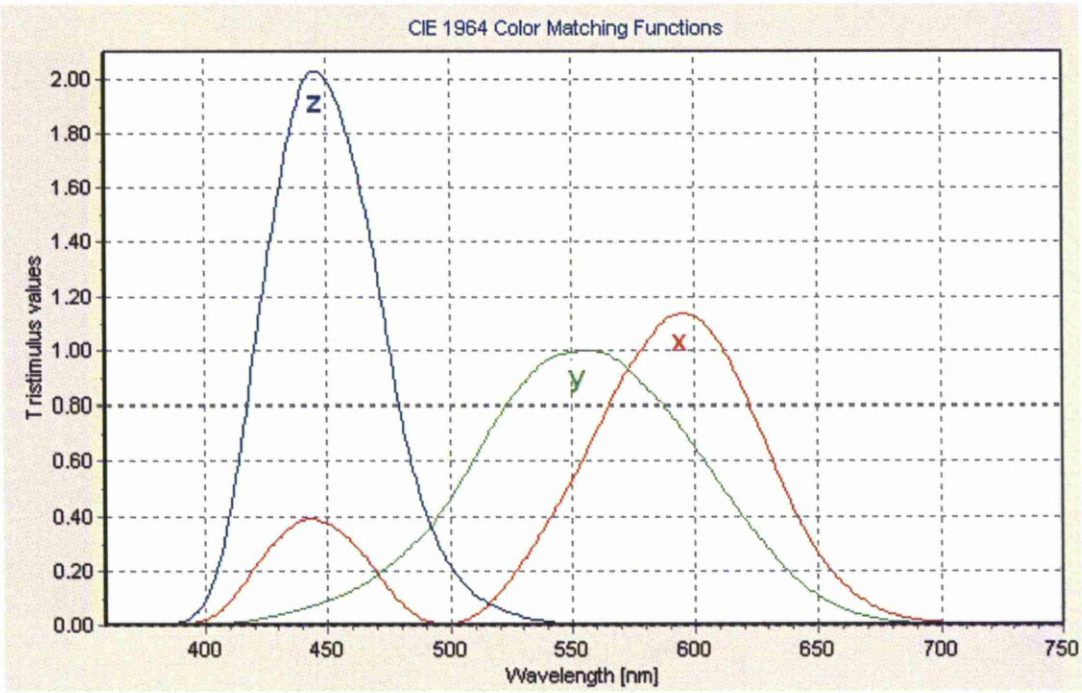


Figure 2-24: CIE 1931 Standardised detectors [37]

The functions are called X, Y and Z. It can be seen that the red function has a second peak towards the lower end of the spectrum. Also, all of the

functions overlap meaning that no light source can stimulate one function alone without stimulating another. This natural process can be implemented in electrical domain by using three opto-electronic detectors, which are simply semiconductor devices that transform light into an electrical signal. This is the basis of the chromatic monitoring system. From these functions a "colour" is defined as the relative stimulus of the eyes X, Y and Z channels. It makes sense to It makes sense therefore to define a colour by an x, y and z triplet which are normalized versions of X, Y and Z:

$$x = \frac{X}{X+Y+Z} \qquad \textbf{2-9}$$

$$y = \frac{Y}{X+Y+Z} \qquad \textbf{2-10}$$

$$z = \frac{Z}{X+Y+Z} \qquad \textbf{2-11}$$

By definition, $x + y + z = 1$ and hence only two out of the three x, y and z coordinates are needed to uniquely define a colour. It is conventional to define

colours by their x and y coordinates. The CIE chromaticity diagram is derived from this, Figure 2-25.

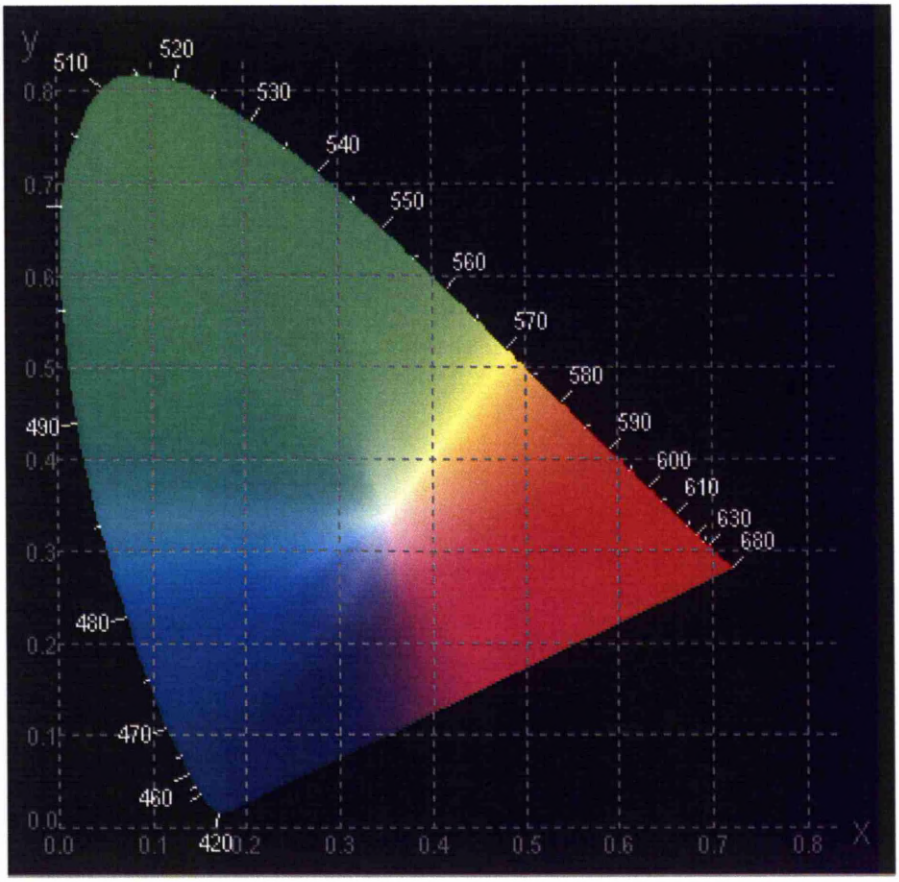


Figure 2-25: CIE 1931 Chromaticity Diagram [38]

This horseshoe shaped space contains all of the possible colours that can be detected by using the CIE standard detector whose functions can be seen in Figure 2-24. The white point in the centre represents the condition when all of the chromaticity values are equal (X = Y = Z = 0.333.).

2.5.5 The HLS Colour Scheme

2.5.5.1 Introduction

The last section described the XYZ colour space, however it can be seen that the distribution of colour is non uniform (horseshoe shape). Various colour spaces with even distributions have been developed; however, in this thesis only the HLS colour space will be discussed. The HLS colour space is the Hue – Lightness – Saturation model. Figure 2-26 gives a visual representation.

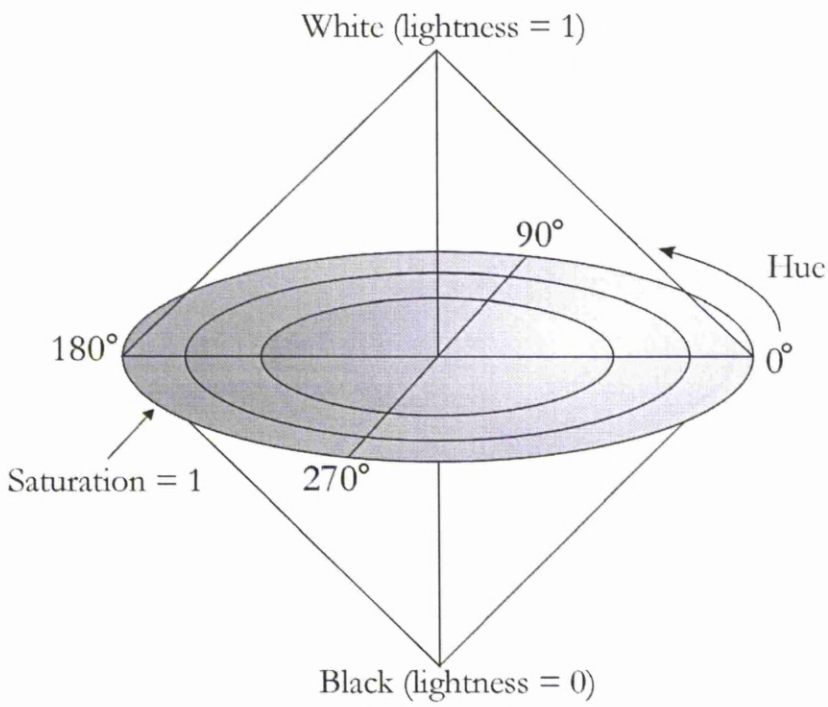


Figure 2-26: The hue, lightness, and saturation model *Anupriya* [40]

The Hue, Lightness and Saturation are calculated using the RGB values.

2.5.5.2 Hue

The Hue is a measure of the dominant wavelength. This project will not describe the mathematics of how the hue equations are derived and will simply present them. The hue (H) is calculated. By first calculating the r, g and b values where,

$$[r,g,b]=[R,G,B]-\min(R,G,B) \qquad \textbf{2-12}$$

One of these values will always be zero.

The following decision tree is then used, *Dean* [39].

If	Then	
$r = 0$	$H = 240 - 120\left(\frac{g}{g+b}\right)$	
If	Then	
$g = 0$	$H = 360 - 120\left(\frac{b}{b+r}\right)$	**2-13**
If	Then	
$b = 0$	$H = 120 - 120\left(\frac{r}{r+g}\right)$	

2.5.5.3 Lightness

The Lightness is a measure of the brightness and is calculated using the following:

$$L = \left(\frac{\max(R,G,B) + \min(R,G,B)}{2} \right) \qquad \textbf{2-14}$$

2.5.5.4 Saturation

The Saturation is a measure of the depth of the colour and is calculated using the following:

$$S = \frac{(\max(R,G,B) - \min(R,G,B))}{(\max(R,G,B) + \min(R,G,B))} \qquad \textbf{2-15}$$

2.5.5.5 HL and HS polar plots

In order that data can be viewed easier, the HLS three dimensional colour space in Figure 2-26 can be represented using two 2-dimensional polar plots, Figure 2-27.

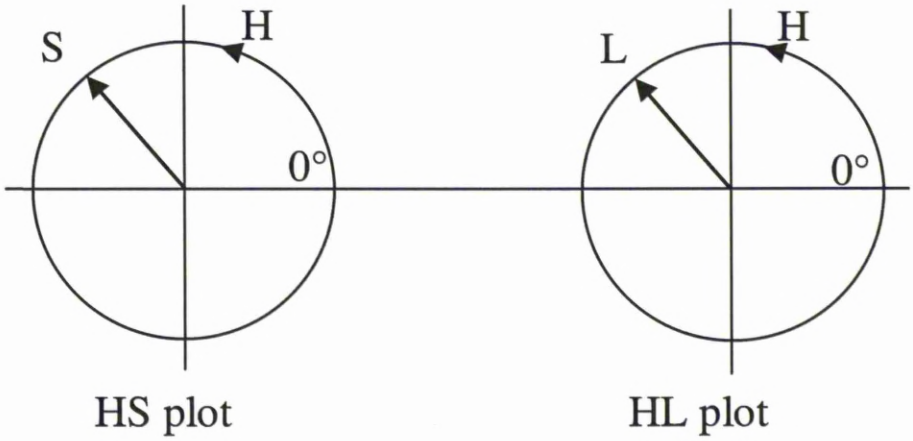


Figure 2-27: HL and HS Polar plots

Any point in HLS space can be represented using the two plots. As expected the Hue angle will be the same for each plot. It is the distance from the centre of the plot which will change depending on whether it is Saturation of Lightness being recorded. These two plots can be easily used to detect changes in the measured systems.

2.5.6 Identification of emergent patterns

The method described in section 2.5.5 can be applied to a number of different applications. A useful application is that of data compression. Figure 2-28 shows a random signal along with three non orthogonal Gaussian functions that are similar to the detectors in Figure 2-24.

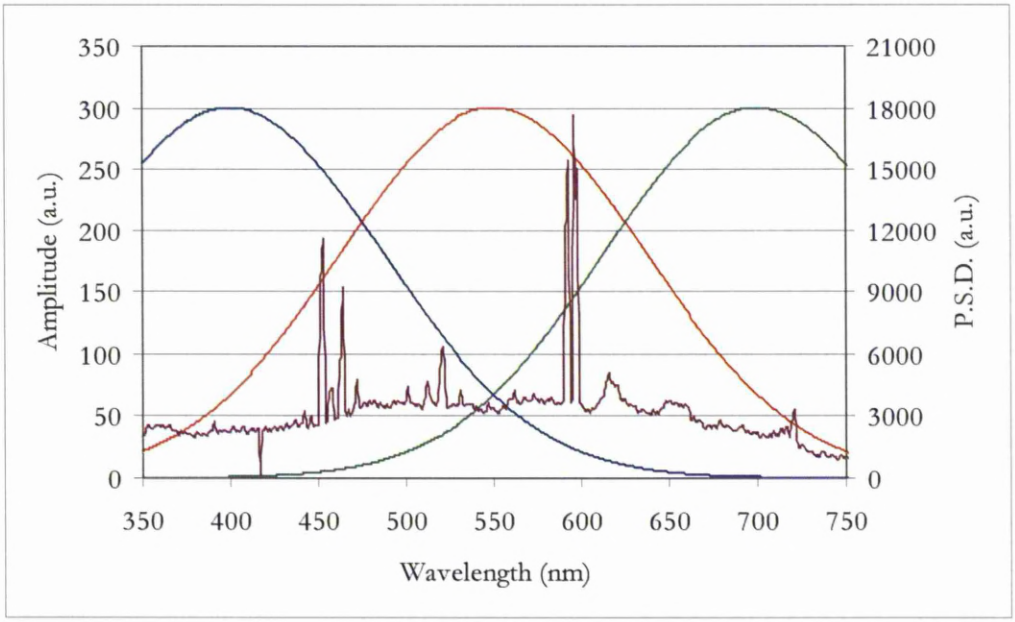


Figure 2-28: Random signal and filter

The three functions above are different to the CIE standard functions in Figure 2-24, however this is a chromatic space and not a colour space so the functions above are acceptabel and do not need to conform to the CIE standard. The only proviso is that the responses overlap. Integrating the functions and signal together leaves three values, which shall be called R, G and B that can then be plotted on H-L and H-S polar plots. Figure 2-29 shows an example of 3 signals t_1, t_2 and t_3. The three signals are compressed into three points on one polar plot. The above example can also be performed using three triangle functions instead of non orthogonal functions and can be applied to any non optical signals also.

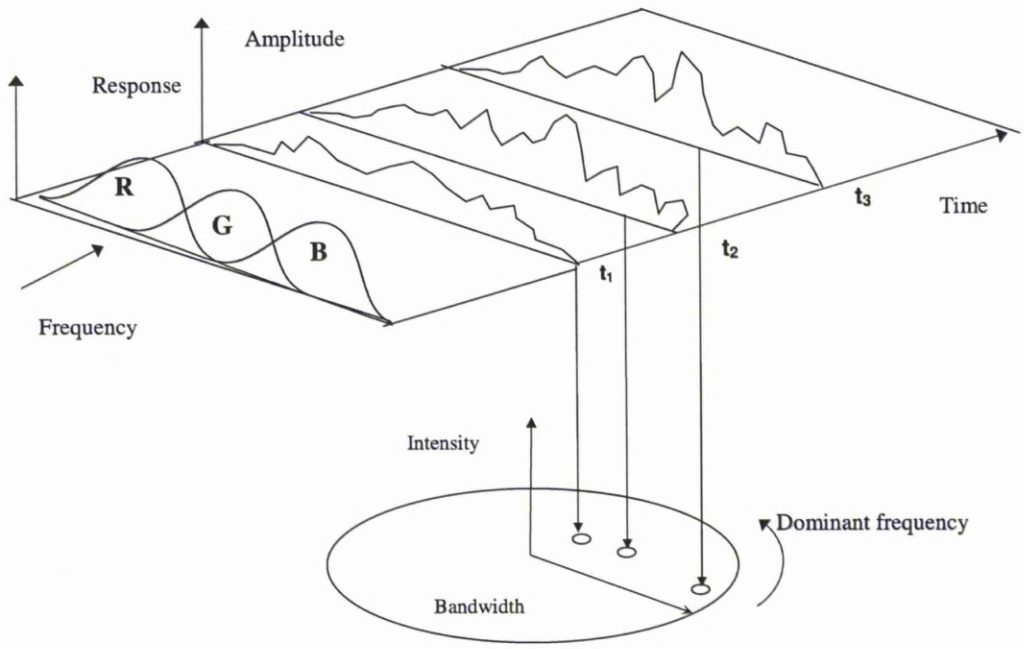


Figure 2-29: Data Compression

Each point can represent very complex changes in systems. The example above uses a signal between wavelengths 350 nm to 750 nm. However, this technique can be used in the acoustic domain, *Dean* [39]. It can also be used to detect transformer failures using gas masses, *Zhang* [41]. This technique is very versatile and has also been used in the time, frequency and space domains to name a few. This project is only concerned with the atomic mass and space domains.

2.5.7 Type of Filter

The previous example above uses Gaussian filters and they can be optimised The best linearity occurring when the individual filters are spaced 2σ apart and the best linearity is obtained by the use of truncated triangle filters *Dean* [42], Figure 2-30.

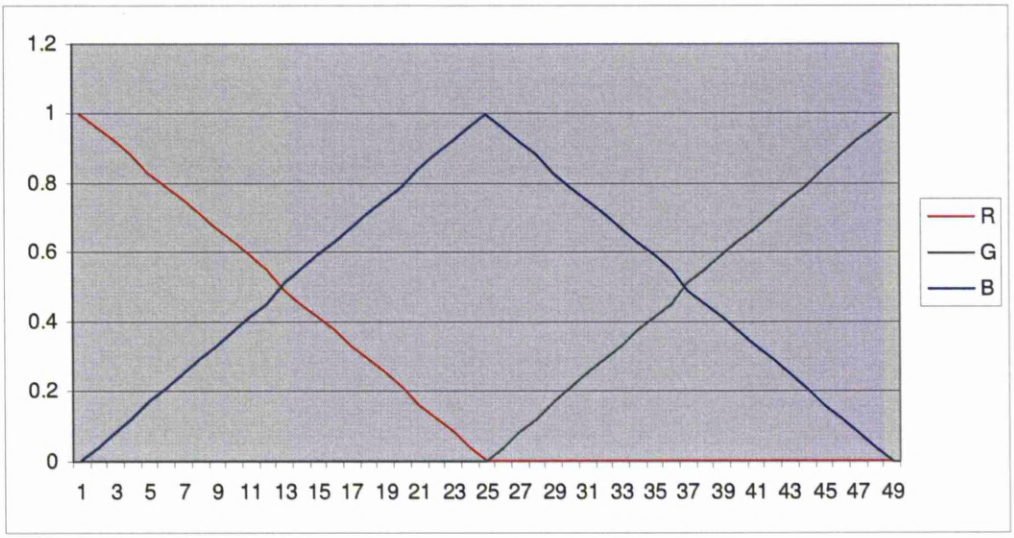


Figure 2-30: Triangle Filter

In the above example the y-axis is normalised to values between 0 and 1 and the x-axis between 0 – 50. When applying this filter to a set of data, the values the x and y axis' take depend entirely on the values of the data being observed. The units of the x-axis and y-axis will depend on the domain that is being used.

2.5.8 Normalisation

When using the chromatic technique it is useful to normalise the values so that the maximum saturation/lightness values are at the circumference and the minimum values are at the centre of the polar plots. The hue value is already normalised so that maximum and minimum hue are at 360° and 0° respectively. The Lightness and Saturation values vary between 0 and 1. The reason for doing this is so that the data covers the maximum area of the plot possible in order that the data can be visualised more accurately. When transferring the chromatic technique to a domain other than the optical domain, the chromatic parameters H, L and S do not refer to a Hue, Lightness and Saturation value. Therefore, in this project the technique when applied to RGA scans for partial pressure versus atomic mass the "H" value refers to the dominant mass rather than the dominant wavelength as is normal for an optical signal. The importance of the Lightness and Saturation values are discussed in more detail in chapter 5.

2.5.9 Application to RGA Mass Spectra

2.5.9.1 Introduction

The following section describes how chromatic techniques are applied to the mass spectra produced by an RGA. A set of filters is applied to the mass spectra data. This aids identification of emergent patterns. The tri-stimulus

methodology is then applied in the spatial domain using single atomic mass unit peaks and the spatial distribution.

2.5.9.2 Fixed Filter

The following RGA scans show the comparison between a sample of ambient air and a sample taken from the air inside a balloon that has been blown up, Figure 2-31 and Figure 2-32. There are differences between the scans.

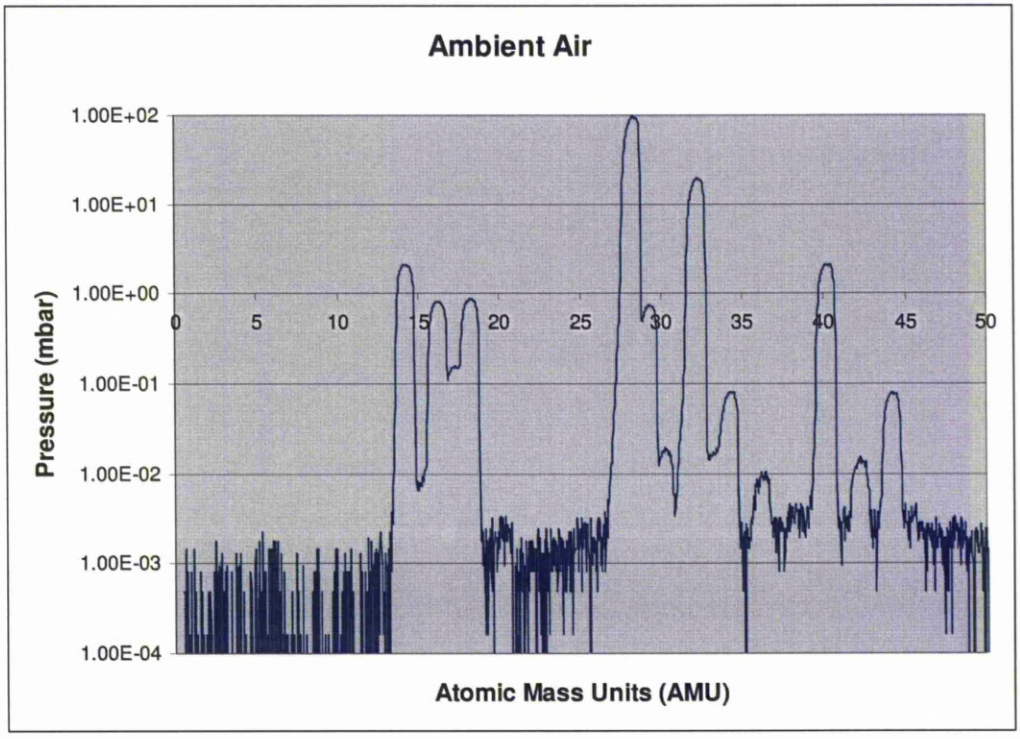


Figure 2-31: RGA Scan of Ambient Air

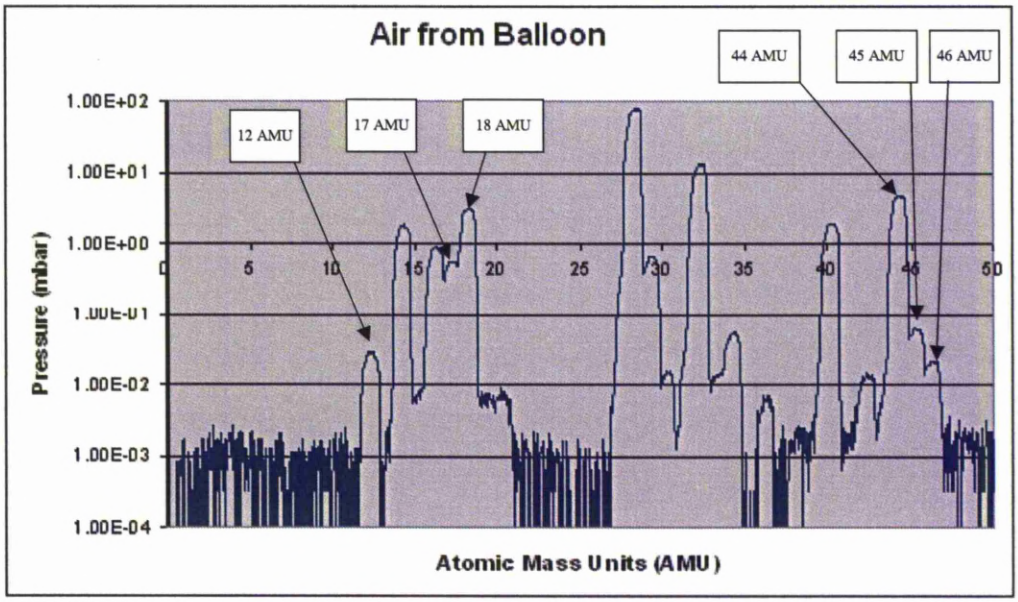


Figure 2-32: RGA Scan of the air inside a balloon

The balloon has been blown using human breath and therefore it will contain more CO_2 and water than the sample of ambient air. The peaks representing this change can be seen most clearly at AMU's 12, 17, 18, 44, 45 and 46. If it was not known where the sample had been taken from it could be difficult to understand what had caused the changes.

The triangle filter of Figure 2-30 is applied to each of the RGA scans and the following H-L and H-S plots are obtained, Figure 2-34 and Figure 2-33. It can be seen that the placement of the data for each of the different scans is in a different part of the plot. Every data point inside the circular polar plot will

represent a different pattern. It can be seen that for a subtle change in the pattern from ambient air to balloon air a change in the polar co-ordinates is observed..

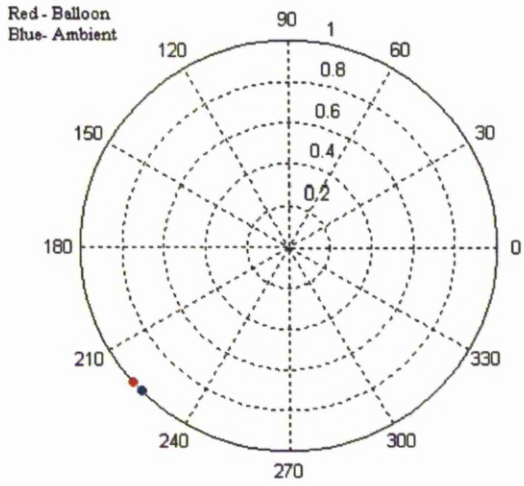


Figure 2-33: H-S Plot

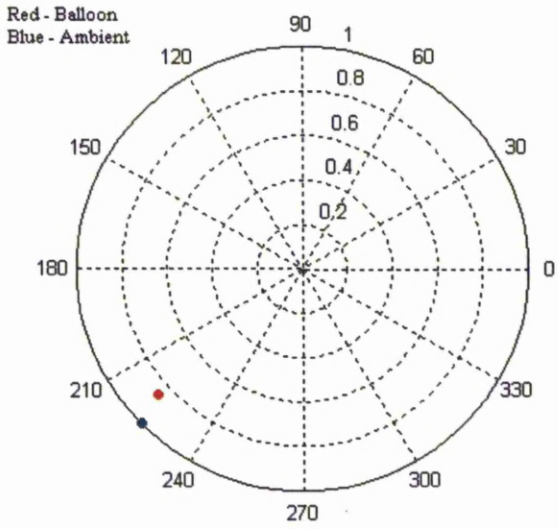


Figure 2-34: H-L Plot

The triangle filter was also applied to the ambient air scan after it had been shifted by 0.5 AMU. The Lightness and Saturation remained at a value of 1 whilst the Hue changed by approximately 4 degrees indicating that this technique could therefore be applied to more complex mass spectra in order to identify emergent patterns.

2.5.9.3 Stepped Filter

The stepped filter is a variation on the fixed filter described above. The same triangle filter is applied to the RGA data spectrums but is stepped along the scan, Figure 2-35.

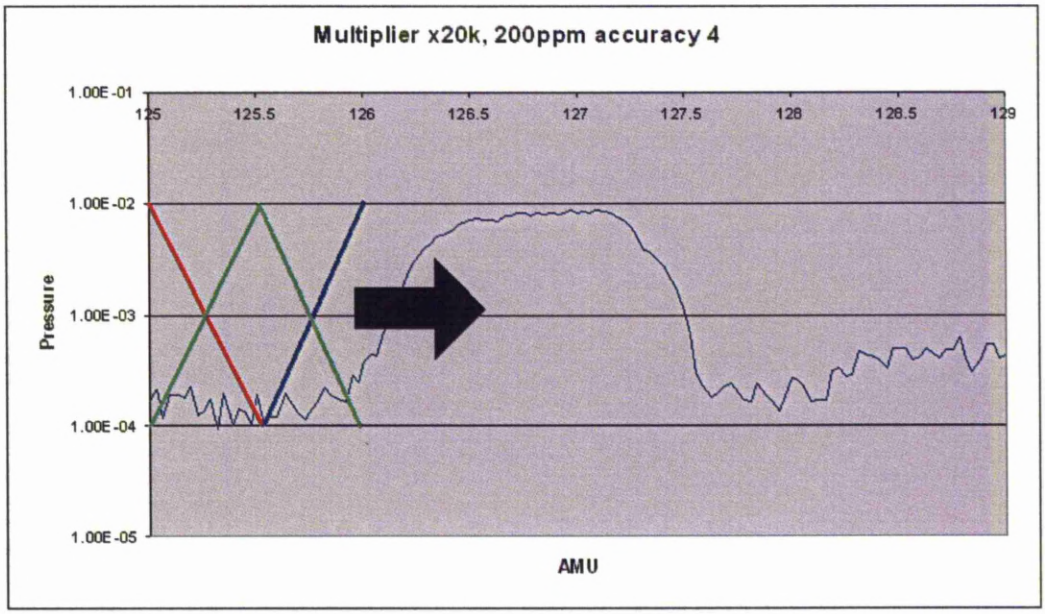


Figure 2-35: Stepped Filter

Multiple values for Hue, Saturation and lightness values are obtained using this method which can be presented using H-L and H-S plots. The plots will have a start point and an end point and the amount of data can vary depending on filter size, step size and the length of data the filter is to cover. In Figure 2-35 the triangle filter is 1 AMU wide and the start point is 125 AMU and the end point is 128 AMU with a step of 0.5 AMU. This means that there are 7 data points on the corresponding H-L and H-S plots. The application of this will be explored later.

2.5.9.4 Spatial

The following describes how the chromatic technique can be used in the spatial domain by using three measurement points A, B and C in a predefined space, Figure 2-36.

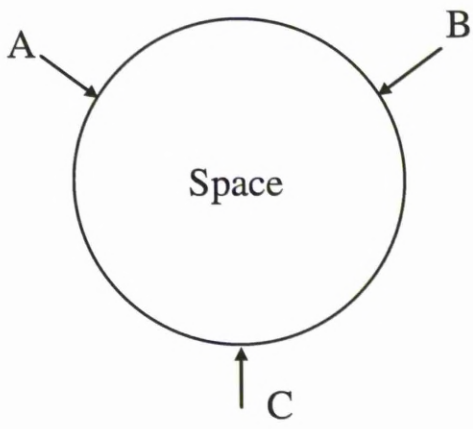


Figure 2-36: Tri Measurement diagram

Measurement points are positioned exactly 120° apart from each other and the diameter of the space can be changed respective of the application. In this project the measurand is gas concentration and the measurement device is a mass spectrometer. Measurements are taken at each point after which the values are normalised to the maximum concentration noted throughout testing. The values taken at points A, B and C are then used as R, G and B values and processed as chromatically in order that an H-L and an H-S plot can be produced. The plots that are produced can be interpreted in a number of ways. This technique is discussed in more detail in further chapters.

2.6 Conclusions

A comprehensive review has been given of the circuit breaker, Sulphurhexaflouride and methods of detecting it. A gas dispersion model has been discussed along with the chromatic process. The three methods of modelling that are used in the smoke stack industry have been explained but have been found to be too complicated to apply to small scale leaks. The variables in the three smoke stack equations would maybe have to be taken into account if SF_6 was monitored outdoors over large areas. A simple version of the Gaussian model can be used to find the position of a leak using three detectors. Chapter 4 discusses experiments in the laboratory using a tri-stimulus sampling system to monitor a known leak. This data is used to determine the dispersion coefficient.

A review of chromatic monitoring has also been given and it has been shown how it is possible to transfer the techniques that are used in these methods into different domains. The following chapters explain how the chromatic technique is used in the atomic mass and spatial domains.

2.7 References

[1] Siemens, *High Voltage Circuit breakers*, this page was taken from the Siemens website, available online: https://www.energy-portal.siemens.com/static/us/en/products_solutions/1544_sps2.html

[2] Kema *(2008),* Photograph taken from KEMA's official homepage: http://www.kema.com/

[3] V. N. Maller, M. S. Naidu, *Advances In High Voltage Insulation and arc interruption in SF_6 and Vacuum*, published by Pergamon Press 1981

[4] G. Frind, R. E. Kinsinger, R. D. Miller, H. T. Nagamatsu, H. O. Noeske, *EPRI EL-284, project 246-1, Final report*, January 1977

[5] L. G. Christophorou, J. K. Olthoff, and D. S. Green. *NIST Technical Note 1425*, November 1997

[6] C. J. Dore, J. W. L. Goodwin, J. D. Watterson, T. P. Murrells, N. R. Passant, M. M. Hobson, K. E. Haigh, S. L. Baggot, S. T. Pye, P. J. Coleman, K. R. King, *UK Emissions of Air Pollutants 1970 to 200*, UK National Environmental Technology Centre:2003. 4-10

[7] IPCC, *Climate Change 1995*. The Science of Climate Change. Contribution of Working Group 1 to the second Assessment Report of the

Intergovernmental Panel on Climate Change. Ed. Houghton, JT, Cambridge University Press. 1996.

[8] J. Gribbin, *Hothouse Earth : The Greenhouse Effect and Gaia*, Bantam Press 1990: pp 1

[9] International Council on Large Electrical Systems (CIGRE). *SF_6 Recycling Guide.* Publication number 117; task force 23.10.01 August 1997

[10] ICF Consulting, *Byproducts of Sulfurhaxafluoride (SF_6) Use in the electrical power industry*, prepared for U.S. Environmental Protection Agency, January 2002. contract No. 68-W5-0068, work assignment No. 0005AA-83.

[11] National Library of Medicine (NLM), *Hazardous Substances Databank (HSDB).* Internet site http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB 2001

[12] Air Liquide, *Sulphur Hexafluoride safety data sheet* 2002, Attached in appendices.

[13] Hans-Joachim Hübschmann, *Handbook of GC/MS fundamental applications*, Wiley-VCH. 2001

[14] T. Powell, D. W. Hill, *Non-Dispersive infra-red gas analysis in science, medicine and industry*, Adam Hilger Ltd, 1968. pp 1

[15] F. W. Aston, A magnetic mass spectrometer. Phil Mag. 1919;38pp:707-712

[16] A. J. Dempster, Positive-ray abundance. Phys Rev 1918;11:pp316-321

[17] J. Watson, Introduction to mass spectrometry. Lippincott – Raven 1997 pp 65

[18] J. R. Trainor, P. J. Derrick, Sectors and tandem sectors. Mass Spectrometry in the Biological Sciences: A tutorial. Kluwer academic Publishers 1992:pp3-27

[19] Wong, S. H. Philip, *"Ion Trap Mass Spectrometry"*, Bio analytical Systems. http://www.currentseparations.com/issues/16-3/cs16-3c.pdf [2008]

[20] Tissue, Brian M, *"Time of flight Mass Spectrometry"* , from educational hypermedia:http://elchem.kaist.ac.kr/vt/chem-ed/ms/tof.htm1996.

[21] Stanford Research Systems, *Models RGA100, RGA200, and RGA300 Residual gas analyser instructions manual*, Revision 1.2, October 1996

[22] MKS Instruments, Spectra products, *CIRRUS (LM99) user manual* LP101020.102 2005

[23] The Shodar Education Foundation Inc, *Background reading for Ionization Enerygy,* Available online 2008: http://www.shodor.org/chemviz/ionization/students/background.html

[24] NIST, National Institute of standards and technology, *Chemistry Web book, NIST Standard reference database number 69.* March 2003 (http://webbook.nist.gov/chemistry/)

[25] J. H. Batey, V. G. Quadrupoles Limited, *Quadrupole gas analysers*, Pergamon Journals, Volume 37, pp 659-668: 1987

[26] M. W. Ackley, U. Salil, Himanshu Saxena, *Application of natural Zeolites in the purification and separation of gases*, Microporous and mesoporous materials 61 (2003) pp 25-42, October 2002

[27] J. W. Holbeach and M. R. Davidson, *Eulerian model for dissolution and dispersion of particles entering a liquid*, Third international of conference on CFD in the minerals and process industries, December 2003

[28] P. Zannetti, *Air Pollution Modelling*, computational mechanics publications, 1990 pp 185

[29] R. Barratt, *Atmospheric Dispersion Modelling*, An Introduction to Practical Applications, Earthscan Publications Ltd, 2001 pp 50

[30] SMARTE, Sustainable Management Approaches and Revitalization Tools – electronic, Environmental organisations Web page: http://www.smarte.org/smarte/resource/sn-units-of-measure.xml

[31] G. R. Jones, P. C. Russell, *Chromatic based metrology*, Pure Appl. Opt. 2 (1993) pp 87 – 110.

[32] Keyence (UK) Ltd, Photograph taken from website: http://www.keyence.co.uk.

[33] G. R. Jones, *Plasma monitoring using chromatically processed optical signals* Proc. XXI Int. Conf. on Phenomena in Ionised Gases III (invited lectures) (Bochum) pp 24-33. 1993

[34] A. H. Lu Li, *Wavedriver Battery Fault analysis Using Chromatic sensing*, M.Sc. dissertation. At the University of Liverpool 2001

[35] J. Zhang, *Chromatic identification of incipient transformer failures due to partial discharges* Ph.D. Thesis at the University of Liverpool 2003

[36] E. M. Dean, *Non-intrusive passive acoustic monitoring of liquid flow systems*, Ph.D. Theses , The University of Liverpool 2003, pp 3.11

[37] W. A..Steer, Techmind, *Introduction to colour science*, http://www.techmind.org/colour/ 1 November 2004

[38] F. Glynn II, Overland Parks, *efg's Computer Lab*, available online: http://www.efg2.com/Lab/ July 2005.

[39] E. M. Dean, *Non-intrusive passive acoustic monitoring of liquid flow systems*, Ph.D. Theses , The University of Liverpool 2003, pp 3.23

[40] S. Anupriya, "*Multi-Sensor Data Fusion for Aircraft Fuel Systems using Chromatic Processing*", PhD. Thesis, the University of Liverpool, 2001

[41] J. Zhang, G. R. Jones, A. Deakin, J. W. Spencer, *Chromatic processing of DGA data produced by partial discharges for the prognosis of HV*

transformer behaviour, Institute of physics publishing, Measurement Science and Technology 16 (2005) 556-561

[42] E. M. Dean, *Non-intrusive passive acoustic monitoring of liquid flow systems*, Ph.D. Theses , The University of Liverpool 2003, pp 3.37

Chapter 3 – Experimental Setup & Preliminary tests

This Chapter describes how gas samples are prepared and obtained, it is also explained how the mass spectrometers are used to obtain data. Each mass spectrometer is discussed separately as they operate slightly differently to each other. Typical background mass spectra are analysed and each peak is identified. An "ideal" ambient scan is presented and it is shown how gas samples can be isolated from normal ambient air mass spectra.

3.1 Introduction

An important part of analysing gases using mass spectrometers is the preparation of samples. Difficulties arise when the location of samples are positioned in areas which are inaccessible. This means that it may not be possible to locate a mass spectrometer close to a sample point. Therefore, either an additional capillary tube must be used to access these areas or a sample must be taken from the area and then fed into the mass spectrometer for analysis. The following chapter gives examples of how samples have been handled and also how the mass spectrometers were used to measure gases remotely. The methodology used at the beginning of the investigation is simplified in order to

define the problems with deploying the method. The methodology was then modified in order to improve the sample quality and accuracy in measurements.

3.2 Gas sampling techniques on-site with RGA300

3.2.1 Introduction

One of the main difficulties when using a mass spectrometer for detecting gas leakage over a wide area at a high voltage substation is the transit time for the gas to be moved from the sampling point to the sampling unit. To accelerate gas movement, three techniques were used.

3.2.2 Sampling technique A

The first sampling technique involves using a length of plastic piping from the required sampling area and connecting it directly to the inlet of the mass spectrometer. The samples migrate along the tube to the inlet due to the small flow of gas arising from the mass spectrometers vacuum system, Figure 3-1. It is assumed that the suction does not disturb the local concentration of the sample.

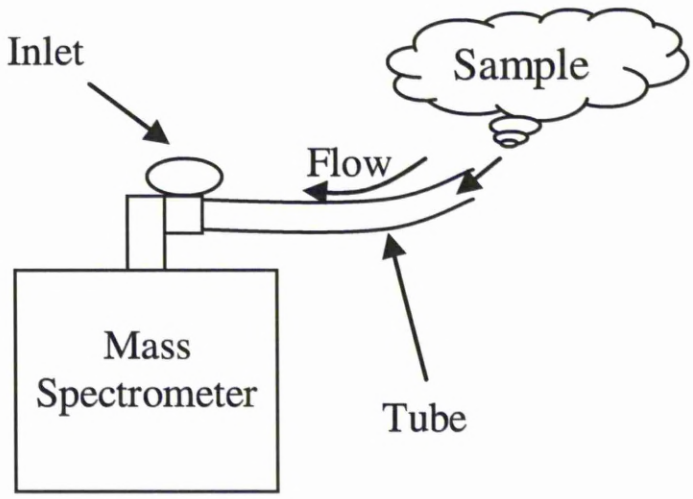


Figure 3-1: Sampling technique A

The problem with this technique is that as the length of the tube is increased then the transit time for gas to migrate along the tube increases. The transit time became substantial (in the order of minutes) with tubing of greater than 1 metre; this was due to the flow rate being small in the order of 50ml/min compared to the volume of the tubing (approximately 78.5×10^3 mm^3 at 1 metre).

3.2.3 Sampling Technique B

The second technique used involved using a plastic piping in tandem with a suction device that was specifically constructed for this project. The suction device was attached to the input nozzle of the mass spectrometer using a T-connector in order that gas is pulled through the pipe inlet of the tube towards the

mass spectrometer. The suction device reduces the transit time for the gas to arrive at the mass spectrometer, Figure 3-2.

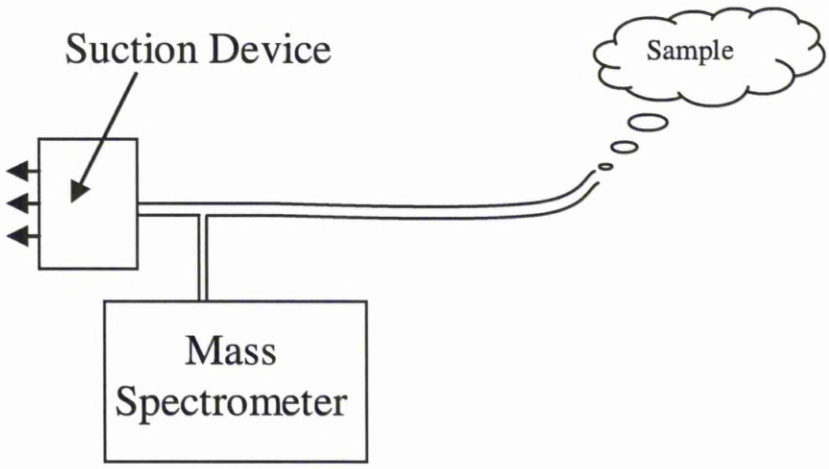


Figure 3-2: Sampling Technique B

A problem with this technique is that the flow rate value for the suction device was greater than that of the mass spectrometer. To overcome this, the suction device was only operated for a couple of seconds in order that the sample can be drawn along the tube and then it was switched off so that the sample could then travel into the mass spectrometer from the T connection point. For longer tubes the transit times were greater. However for a continuous measurement the delay might be acceptable if an SF_6 leak on site was also continuous and not periodic which is what would be expected.

3.2.4 Sampling Technique C

Techniques A and B work fine until the distance between sample point and mass spectrometer becomes large (> 10 metres) and the time for gas transit may be unacceptable for detecting periodic releases of gas. For these instances a method was adopted which involves using the suction device with an attached sample bag. This enables the user to switch the suction device on and obtain a sample gas and then subsequently connect it to the mass spectrometer for analysis, Figure 3-3.

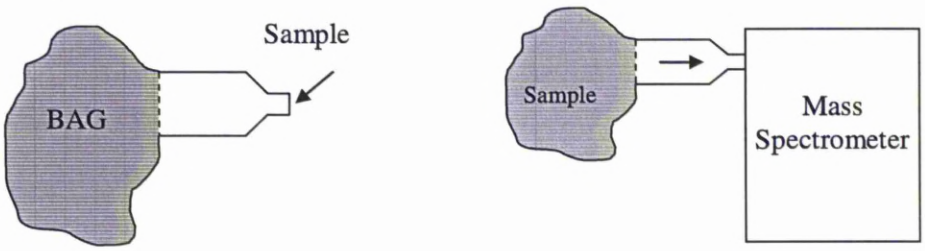


Figure 3-3: Sampling technique C

The bag was completely deflated before the suction device was operated and then the inlet was blocked off when the bag was full. The inlet then becomes the outlet when the suction device was connected to the mass spectrometer so that the gas could be analysed. However, this method would be unsuited for "wide area" substation monitoring.

3.3 RGA300 Scans

3.3.1 Ambient Scan

Mass is qualified in atomic mass units (AMU). One AMU is approximately equal to one proton or neutron. This project is concerned only with masses up to AMU 150. A typical result obtained in open air is shown in Figure 3-4.

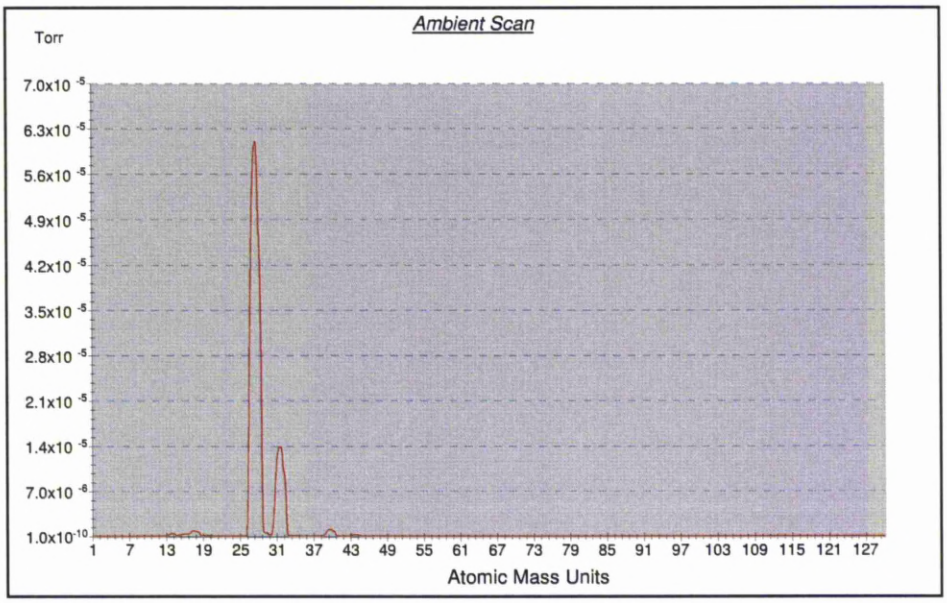


Figure 3-4: Typical Scan of Air

In the figure above there are peaks between 14 and 18 due to ionised species of air (N^+, O^+) and water (O^+, H^+) but they are small and hard to see. The peak at 27 is N_2^+ and the peak at 32 is O_2^+. There is also a small peak at 40 due to

Argon (Ar). Figure 3-4 has a vertical axis set as a linear scale. Large peaks can be seen clearly in linear mode however the peak at 28 (N_2) is much larger than all of the other peaks.

3.3.2 Sulphurhexaflouride Scan

A test was performed in which the mass spectrometer inlet was placed next to the opening of a bottle of pure SF_6. The mass spectrometer was left to continually scan allowing the SF_6 to enter the inlet until the SF_5^+ peak increases and settles at a maximum value. The scan obtained can be seen in Figure 3-5.

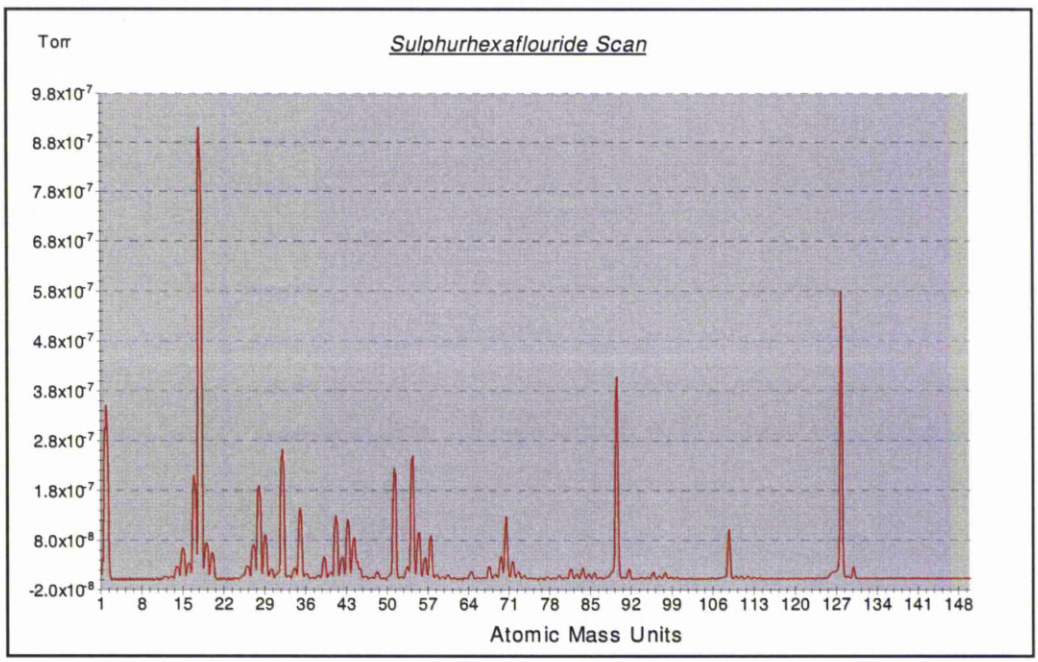


Figure 3-5: Scan of pure SF_6 escaping gas bottle

As expected the scan result shows a mixture of air and SF_6. The additional peaks in the scan are associated with SF_5^+, SF_4^+, SF_3^+, SF_2^+, SF^+, S^+ and F^+ at masses 127, 108, 89, 70, 51, 32 and 19 respectively. Note that there is not a peak at mass 146 (SF_6^+). The reason for this is that the gas has fragmented due to the ionisation process. The energy in the ionisation process was sufficient to break down the SF_6^+ and separate a Fluorine atom. As with Figure 3-4 the vertical axis of Figure 3-5 is set to a linear scale. In this case the SF_5^+ peak is large due to the large concentration of SF_6 in the sample but this peak is much smaller for lower concentrations of SF_6. Another way of viewing the scans from the mass spectrometer is to set the vertical axis to a logarithmic scale.

3.3.3 Logarithmic Scale

For detecting small concentrations of SF_6 that are orders of magnitude below the maximum peak (N_2^+) it is best to set the vertical pressure axis of the mass spectrometer to a logarithmic scale. An ambient scan result (no SF_6) using a log scale can be seen in Figure 3-6.

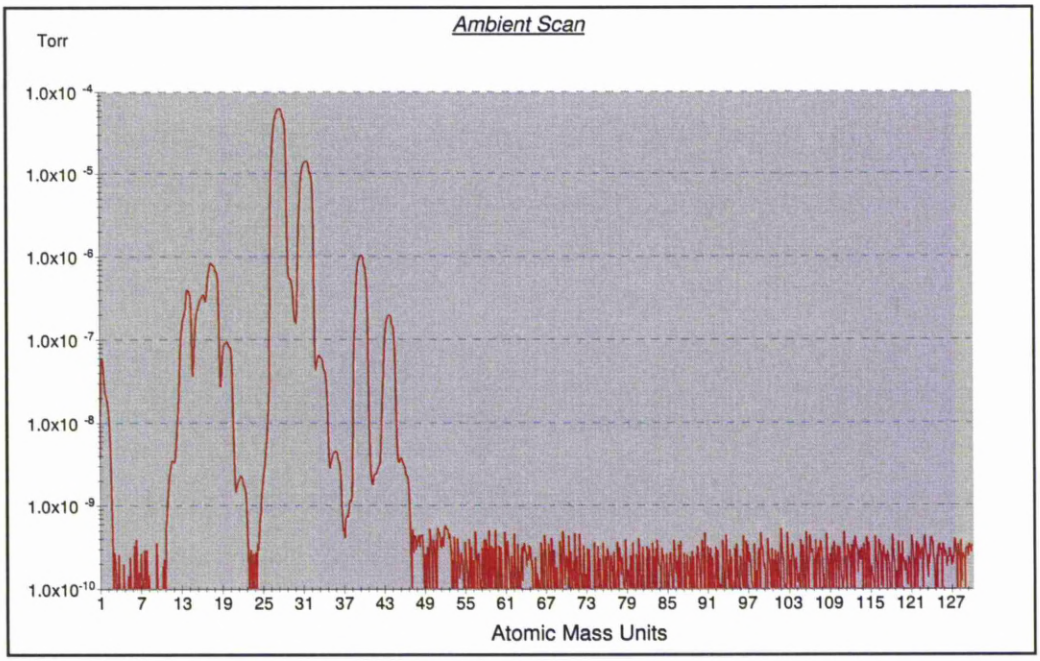


Figure 3-6: Ambient air log scan

The data in this graph compared to Figure 3-4 is much more informative as now the lower concentration gases are visible. For smaller peaks subtle changes can now be monitored more easily. This means that it is easier to identify gas components for particular masses. Some of the peaks in this ambient scan appear to have additional peaks that overlap. The reason for this is that the resolution is such that on a logarithmic scale lower component concentrations become more visible. However since SF_6 is being investigated then the SF_5^+ peak falls outside the mass range for these components and therefore will not cause a problem.

3.3.4 Ideal Ambient Scan

The peaks in Figure 3-6 are produced from a sample of the earth's atmosphere. Below is a table of the composition of the earth's atmosphere.

Element	**Percentage**
Nitrogen	78.1
Oxygen	20.9
Argon	0.9
Carbon dioxide, Methane, Rare (inert) gases	0.1

Table 3-1: Composition of the earth's atmosphere

Figure 3-7 to Figure 3-11 show the mass spectra signature for the elements in Table 3-1. The figures were compiled using values taken from the National Institute of Standards and Technology (NIST) which is run by the U.S. government, *NIST* [1].

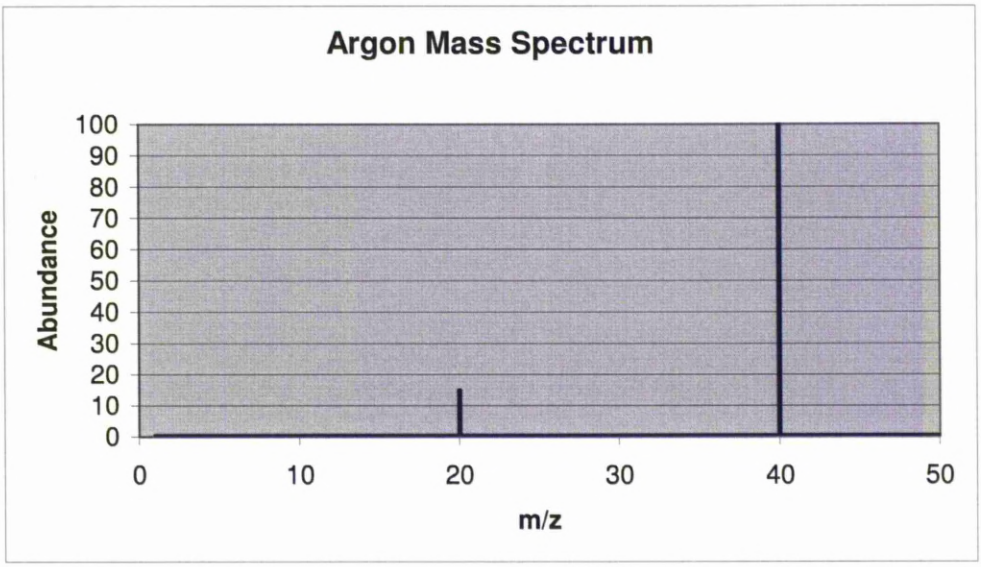


Figure 3-7: Mass Spectrum of Argon

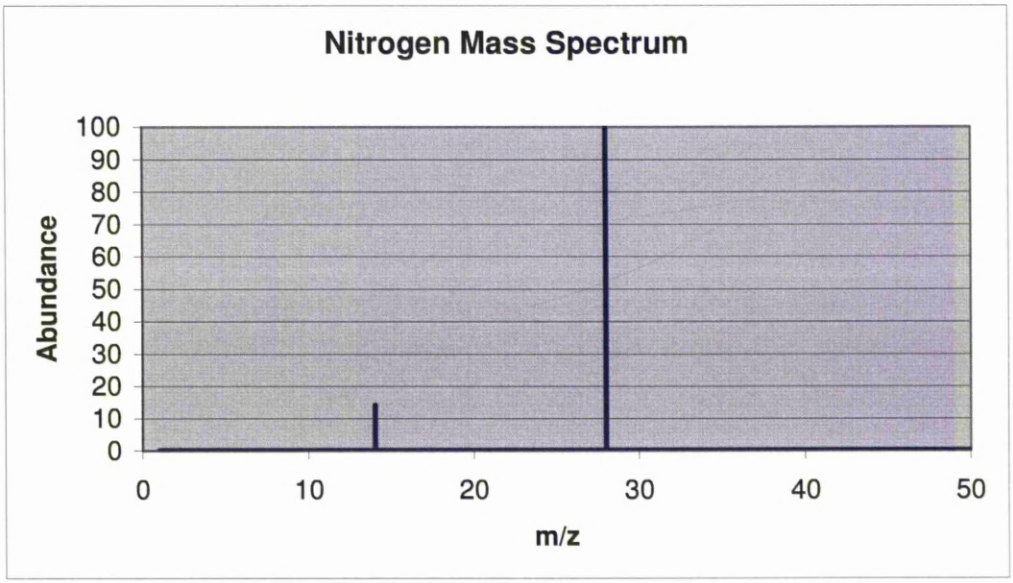


Figure 3-8: Mass Spectrum of Nitrogen

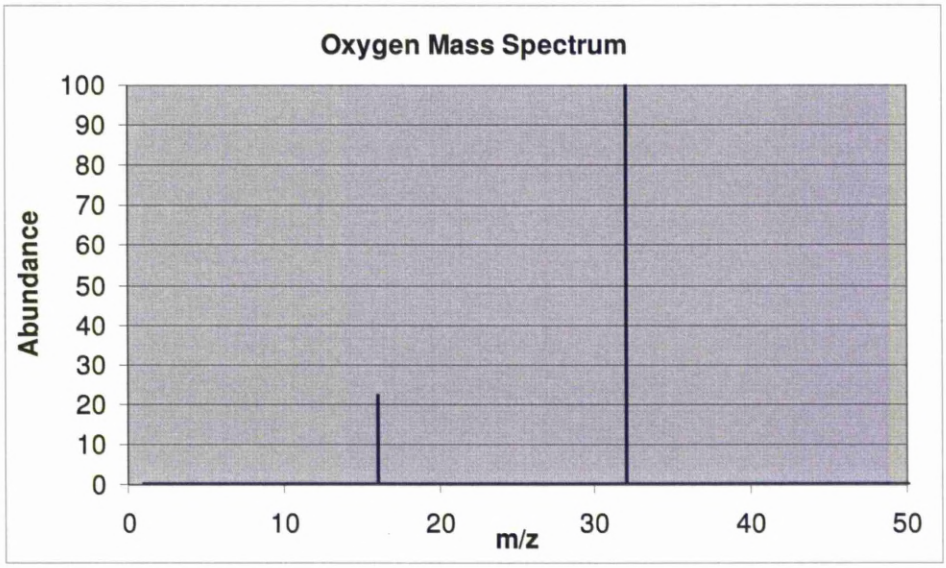


Figure 3-9: Mass Spectrum of Oxygen

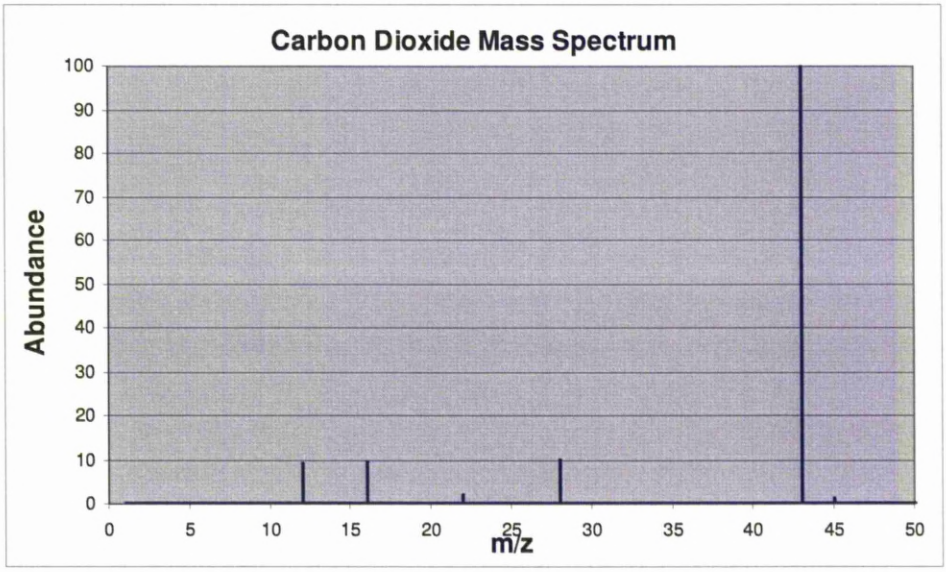


Figure 3-10: Mass Spectrum of Carbon Dioxide

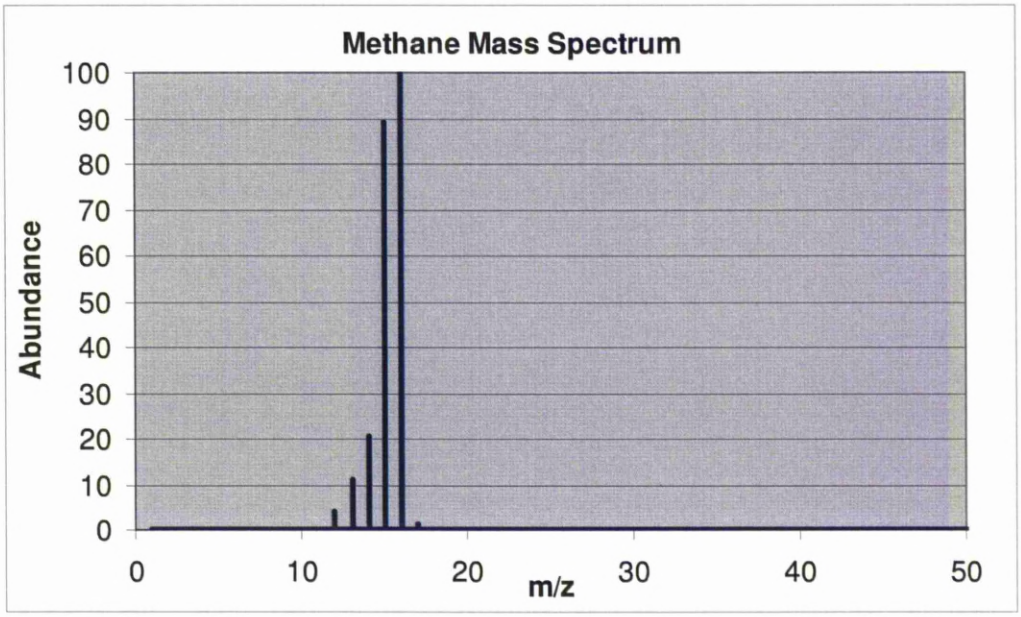


Figure 3-11: Mass spectrum of Methane

The NIST site provides thermo chemical, thermo physical, and ion energetics data compiled by NIST under the Standard Reference Data Program [1]. The spectrums can be combined and integrated using the percentages in Table 3-1 to produce an ideal ambient spectrum, Figure 3-12.

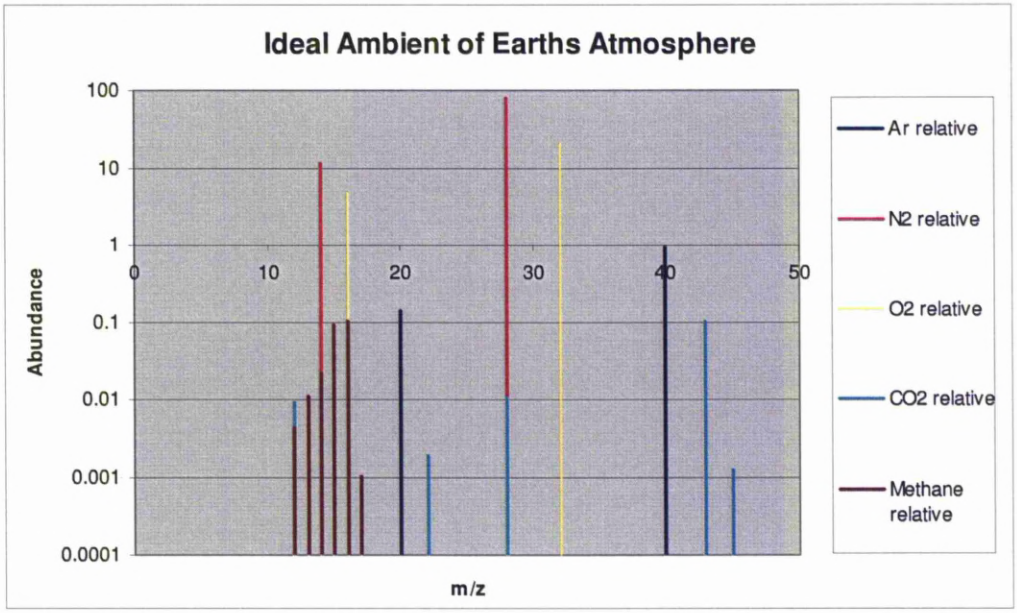


Figure 3-12: Ideal Ambient of Earth's Atmosphere

It can be seen that some of the peaks are buried within other peaks. This ideal scan looks very similar to ambient scan taken using the mass spectrometer and shown in Figure 3-6. The main difference is that there is a large peak at 1-4 AMU. This is an artefact arising from the operation of the spectrometer. When the applied potentials are small (or zero) as at the beginning of a scan, ions entering the filter may be transmitted even though their trajectories are mathematically unstable, just because of the weakness of the fields and the finite length of the filter. This gives rise to an output signal at the beginning of the mass scans. This is a phenomenon called "zero blast".

There are also some other small peaks in the measured scan that differ from the ideal scan. These are due to oil and grease vapours that are inherent in the system. However, these are small enough to be counted as insignificant and may be ignored.

3.4 Gas sampling techniques using the CIRRUS

3.4.1 Introduction

The tri measurement system required a mass spectrometer with more functionality than the RGA300 and therefore a mass spectrometer was purchased from MKS called the CIRRUS which contained an electron multiplier. This meant that a different approach was required when undertaking tests using this apparatus. The CIRRUS Mass Spectrometer has a capillary tube attached which has a very small diameter (0.2 mm); this means that samples enter the mass spectrometer and have a smaller transit time. Also, the resolution of the CIRRUS can be changed and set with more accuracy which means that smaller concentrations can be measured and complex peaks with multiple overlaps can be resolved much easier. When the capillary tube is not sufficiently long enough to reach a sample area an extension must be fitted. The tubing used to provide this extension is also of a small diameter as the one supplied with the unit in order that

the transit time is kept low. Using a smaller diameter also eliminates the need for an external pump as the flow rate of the Mass Spectrometer is sufficient. It should be noted that when using the CIRRUS software, partial pressure values displayed in mBar unlike the RGA300 which uses Torr. 1 mBar equals approximately 0.75 Torr. The software packages associated with each piece of equipment did not allow the user to choose the units and therefore throughout this thesis mBar is used when associated with measurements from using the CIRRUS and Torr is used when discussing measurements taken using the RGA300.

3.4.2 Transit time

The pipes used with the RGA300 had an inner diameter of approximately 3 mm which makes the volume of the pipe relatively large i.e. 215450mm^3 at 7,620mm (25 foot). This affected the time it took for the gas to travel to the Mass Spectrometer and also the quality of the sample. The CIRRUS facilitates the use of pipes with an inner diameter of 0.2 mm which at 7,620 mm gives a volume of 239.4 mm^3. One pipe is connected to the capillary of the mass spectrometer and SF_6 is allowed to migrate into the pipe orifice. The following trace is obtained, Figure 3-1.

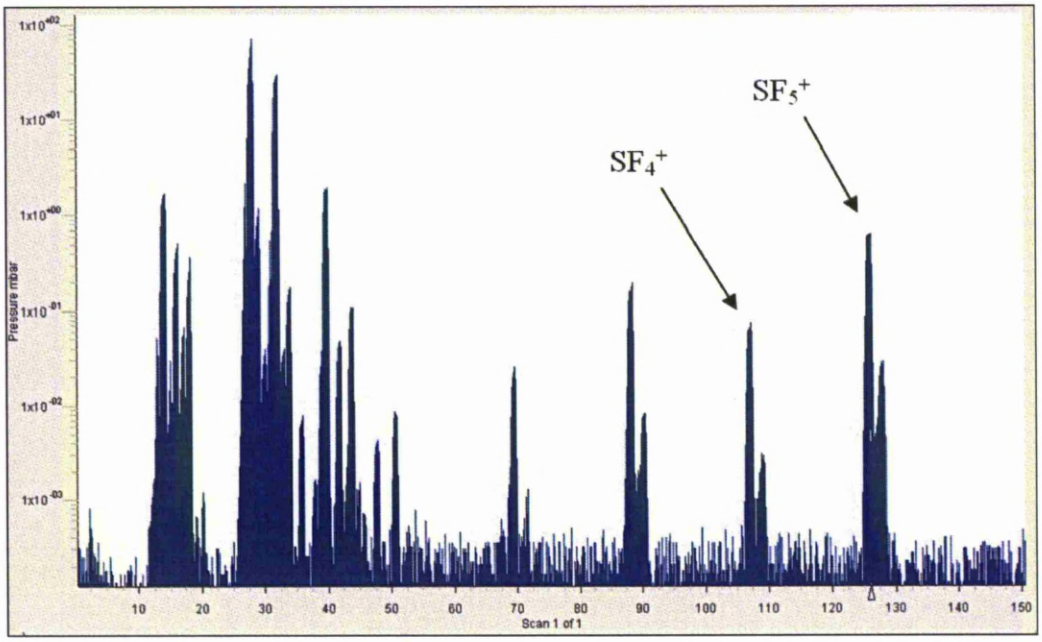


Figure 3-13: SF6 scan data

The SF_5^+, SF_4^+ etc. peaks can be seen very clearly. However it should also be noted that peaks can be seen at mass 129, and next to each SF peak below that. The reason for this is that Sulphur has 4 naturally occurring stable isotopes, ^{32}S, ^{33}S, ^{34}S and ^{36}S. The figure below gives the Natural abundances of each of the Isotopes of Sulphur, Figure 3-14.

Isotope	Atomic mass (mass units)	Natural abundance (atom %)
^{32}S	31.97207070	94.93 %
^{33}S	32.97145843	0.76 %
^{34}S	33.96786665	4.29 %
^{36}S	35.96708062	0.02 %

Figure 3-14: Table of Sulphur Natural Abundances, *Mark Winter* [2]

However, because of the smaller relative abundance of ^{34}S (4.29%) then this means that the $^{34}SF_5^+$ peaks are not as large as the $^{32}SF_5^+$ peaks and they are not considered for the purposes of this project. Furthermore, it can be seen in some of the scans represented in Chapter 4 that these peaks are within the noise level of the mass spectrometer and can not be identified.

The transit time for the peaks to reach a maximum was measured to be approximately 20 seconds after the sample was allowed to migrate into the mass spectrometer, Figure 3-15.

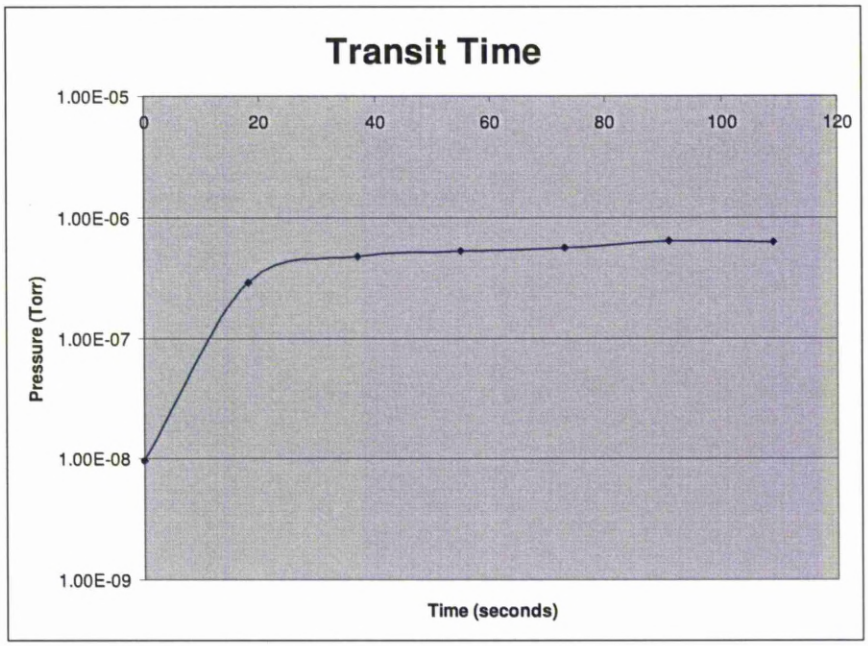


Figure 3-15: SF_5^+ Peak Transit Time

3.4.3 Tri stimulus 2-dimensional set-up

The tri stimulus system incorporates the use of three 0.2 mm diameter, 7,620 mm pipes. A copy of the data sheet for the pipes can be found in Appendix II. Also a Cole-Parmer mixing solenoid valve was used to control the sample flow. A copy of the data sheet for the control valve can be also found in Appendix II. The solenoid valve was used to switch between sample points on the tri stimulus system, Figure 3-16. It should be noted that the scan time was sufficiently fast enough (less than a couple of seconds) not to cause any problems with respect to the transit time.

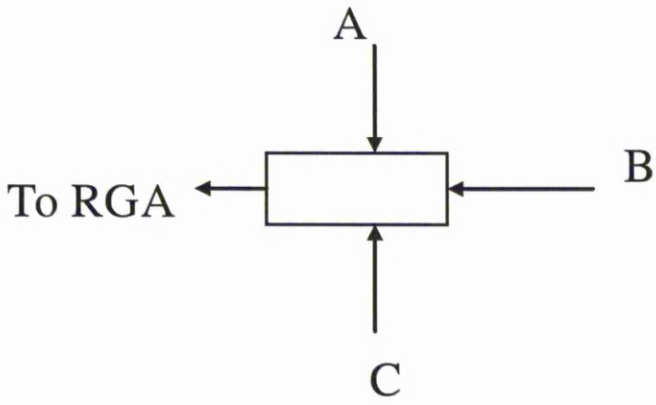


Figure 3-16: Mixing solenoid Valve

3.4.4 Tri Stimulus 3-dimensional set up

The 3-dimensional measurement system consisted of 6 measurement points distributed at 120° apart on the horizontal and vertical axis' meaning that a three input mixing solenoid valve was insufficient. An 8-way Inlet Valve was obtained to cope with the additional 3 measurement points. The valve was manufactured by VICI® and the data sheet can be found in the Appendix. The mode of operation is such that mass spectrometer scans the mass range and then steps the valve around to the next position so that samples can be taken from each connected tube. Valve positions 7 and 8 are switched off as they are not used in the present configuration. All lengths the tubes for each test are kept the same (7,620 mm). Figure 3-17 shows the new Valve and its position.

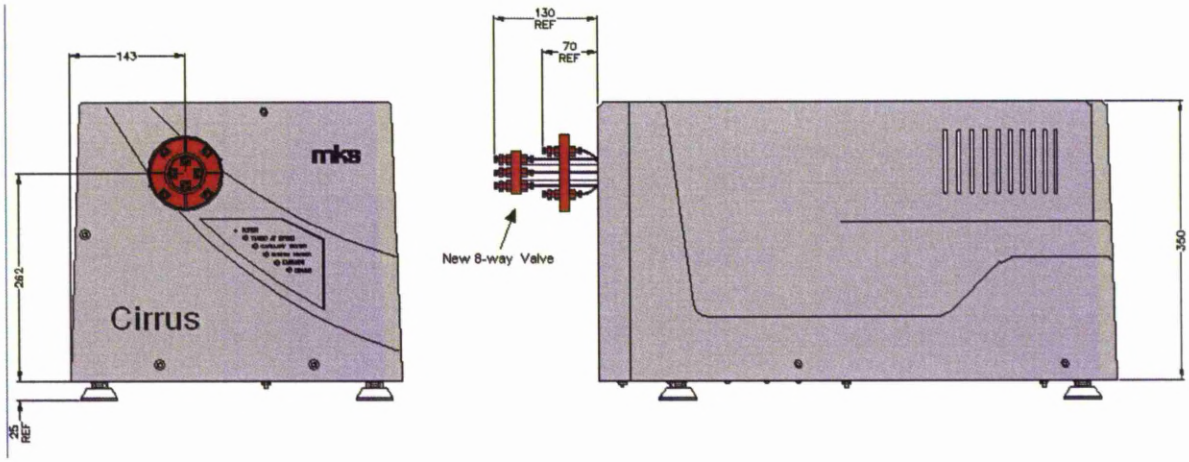


Figure 3-17: New 8-Way Vici® Valve *MKS* [3]

3.4.5 Control of Sampling

The tubes used with the CIRRUS have a small diameter and are relatively long. Therefore, unlike the RGA300 tests, it is not necessary to obtain samples and transport them to the mass spectrometer when using the CIRRUS. The reason for this is because the tubes are long enough to reach the point of measurement and the transit times have been reduced considerably.

The laboratory tests are all completed in a stable environment where air currents will not affect gas movement and therefore produce reliable data. Furthermore, there are tests required in which the concentrations of SF_6 in Air must be known. For these purposes, gas bottles where obtained from CK Gas

products Ltd that contained known concentrations of gas: 20, 50 and 200 ppm SF_6 in air. Certificates are provided and can be found in Appendix III.

3.5 Conclusions

The experimental systems and equipment have been explained in this Chapter. It has been shown that there are a number of different techniques that can be utilised in order that gas samples can be obtained and analysed using a Mass Spectrometer. It has been proven that when analysing small concentrations of gas that a logarithmic scale must be used so that small changes can be monitored more accurately than if using a linear scale. It has also been proven that the transit time from measurement point to measurement unit must be considered and an appropriate pipe or transit method must be carefully selected.

3.6 References

[1] *NIST*, The National Institute of Standards and Technology, web page http://webbook.nist.gov/chemistry/ *© 1991, 1994, 1996, 1997, 1998, 1999, 2000, 2001, 2003, 2005 copyright by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved.*

[2] *Mark Winter*, URL:http://www.webelements.com, Copyright 1993-2007 Mark Winter [The University of Sheffield and Web Elements Ltd, UK]. All rights reserved. Document served: Tuesday 19th February, 2008

[3] *MKS*, CAD drawing provided directly by manufacturers MKS Instruments, 2008

Chapter 4 - Experimental Results

This Chapter reports results taken using both the RGA300 (onsite in Holland) and the CIRRUS (Laboratory tests). The onsite tests consist of mass spectra scans taken near simulated SF_6 leaks at the test station and on actual leaks in a power station. The laboratory tests consist of simulated leaks of known quantities inside a 2 dimensional and 3 dimensional space.

4.1 Introduction

Experiments were performed using two residual gas analysers and associated interpretive software packages. This chapter reports results obtained and also covers calibration of the instruments using known concentrations of SF_6. Calibration tests are undertaken to assess whether SF_5^+ peaks alone can be used to determine concentrations. Also, tests were performed on a two-dimensional and then a three dimensional model using various gases to assess the validity of using such a system to continually monitor for SF_6 leaks.

4.2 RGA300 tests

4.2.1 Introduction

Calibration is an extremely important part of mass spectrometry. If a device is not calibrated then peaks may not coincide with the appropriate AMU values and the partial pressures recorded may not be correct. Also, the partial pressure must be calibrated with known concentrations of gases otherwise the amount of gas in a sample can not be determined. Although mass spectrometry has always been recognized as a technique for quantitative analysis, the interpretation and quantification of the mass spectra is not straightforward. This is for two main reasons:

- The number of peaks that a single gas generates can be more than one (fragmentation).
- The peaks produced by different gases can overlap because the fragments have the same atomic mass numbers (spectral overlap), which can make it very difficult to distinguish between contributions from each of the gases.

A solution to these problems is to use high-resolution mass spectrometers (resolving power larger than 1000) which resolve very close peaks (e.g. ions of N_2^+ and CO^+ which have mass numbers 28.0061 and 27.9949 respectively). However these mass spectrometers are very expensive and are also very bulky

which restrict their use to just a few selected analytical laboratories. Quadrupole mass spectrometers have a lower resolution (resolving power from 100 up to 1000 i.e. can distinguish a peak at 1000 AMU from a peak at 1001 AMU), and are very popular since they are relatively inexpensive, compact and need little experience and training to operate. Due to their limited mass resolution, these spectrometers cannot eliminate the spectral overlap like that seen in chapter 3 and the distinctions between gases are appraised by looking at the secondary peaks of their fragmentation. This project is concerned with the measurement of SF_6 in ambient air. Therefore since the fragmentation peaks (SF_5^+, SF_4^+ etc.) are outside the normal ambient spectra of air (approximately 1 to 60 AMU) then a resolving power of 100 to 1000 is more than sufficient. It is useful to know the concentration of a gas in air. This project will refer to gas concentrations in terms of part per million (ppm). Tests are carried out to see if it is possible to relate any of the fragmentation peaks to the amount of SF_6 present in a sample. The following section describes the calibration procedures for each RGA.

4.2.2 Calibration

4.2.2.1 Introduction

In order that a calibration can be performed, samples of known quantities of SF_6 were required. Flow gauges were used to obtain a number of samples of SF_6 in air. Calibration samples of 45, 83, 168, 330 and 713 ppm of SF6 in air were produced. The RGA300 was connected to the output of the flow gauges using a small length of tube of approximately one metre and the mass spectra were recorded for each sample. The following individual ionised gas components were monitored: SF5+, SF4+, SF3+ and N2+. Figure 4-1 highlights where these peaks appear on a mass spectrometer scan.

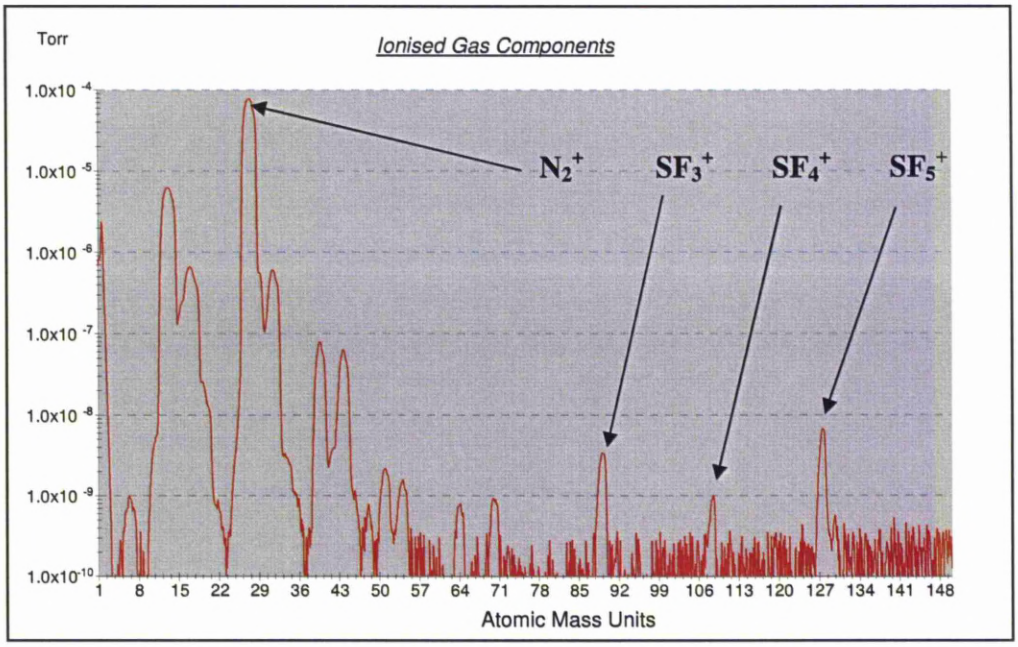


Figure 4-1: Ionised Gas Components

The ionised components that are highlighted were recorded for each calibration sample in order to build a profile at each concentration. The peaks of SF_2^+, SF^+, S^+ and F^+ were not noted as they are either small or are in the region of the spectrum where there are lots of ambient peaks which would require mass discrimination techniques and complicate the calibration procedure.

4.2.2.2 Scan Variation

When the 3 chosen SF^+ peaks (SF_5^+, SF_4^+ & SF_3^+) were monitored using the RGA300 with additional tubing, there was a delay between initialisation of the tests and the point at which the peak stabilised at a maximum value. Peaks appeared small at first as a sample was introduced and then increased until a maximum, this being different for each concentration level. When the sample was removed the peak heights started to decrease slowly and eventually disappear. The reason for the long delay was due to the tubes having a relatively large volume compared to the flow rate of the inlet (≈50 ml/min). Figure 4-2 and Figure 4-3 illustrate how the SF_3^+, SF_4^+ and SF_5^+ peaks increased over 8 minutes.

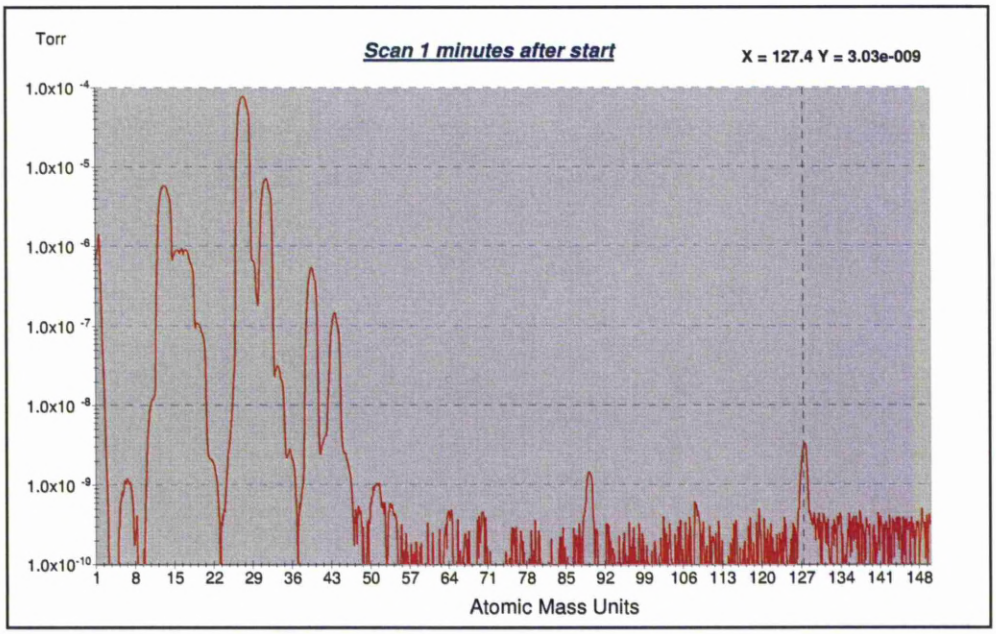


Figure 4-2: One minute after start

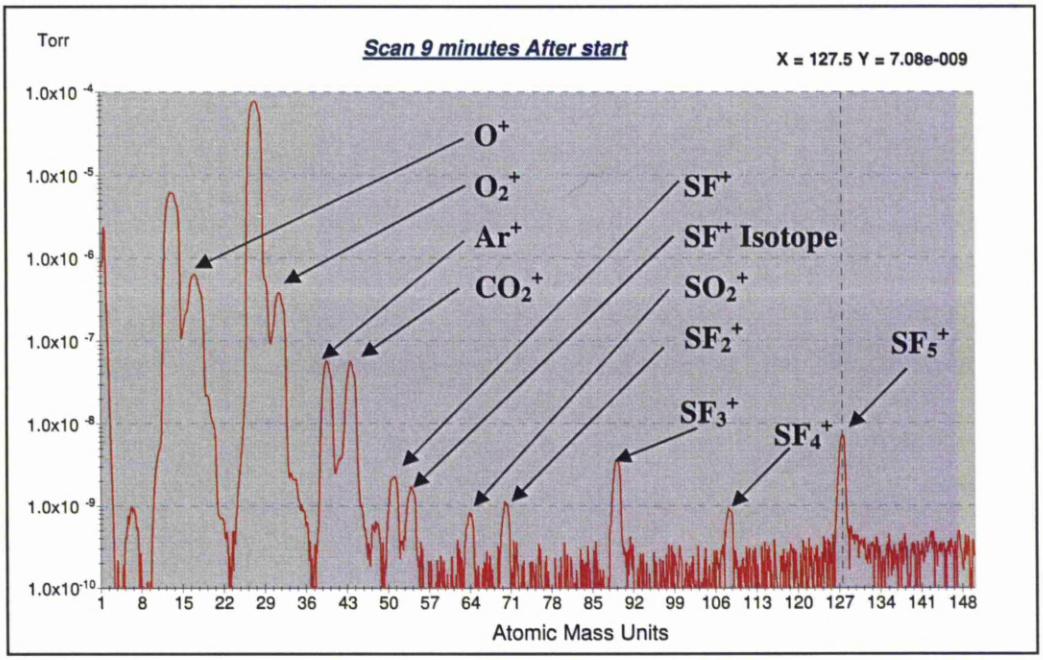


Figure 4-3: Nine Minutes after Start

The time it takes for a peak to reach its maximum depends on the volume of the sampling tube and the flow rate of the measurement device. The RGA300 permitted a tube of diameter 3 mm. The flow rate depends on the vacuum system and inlet size and is in the order of 50 ml/min. When a small diameter (0.2 mm) capillary tube is used on the CIRRUS the transit time is dramatically reduced because of the reduction in the volume of the tube. As well as the SF_3^+, SF_4^+ and SF_5^+ peaks, other changes can be seen between Figure 4-2 and Figure 4-3. The changes are highlighted on Figure 4-3. The increase in the pressure peaks highlight on the graph as SF^+, SF^+ Isotope, SO_2^+ and SF_2^+ are due to SF_6. The reduction in the pressure peaks highlighted as O^+, O_2^+, Ar^+ and CO_2^+ are due to their concentrations in the sample reducing because of the presence of SF_6.

4.2.2.3 Calibration Data Analysis

The partial pressure peak value at SF_5^+ is the largest of the fragmented peaks of SF_6 and that this peak would be the most suitable to monitor for small concentrations of SF_6. The maximum SF_5^+ peaks expressed as partial pressures taken from the data collected for different concentrations of SF_6 in air are shown in Figure 4-4.

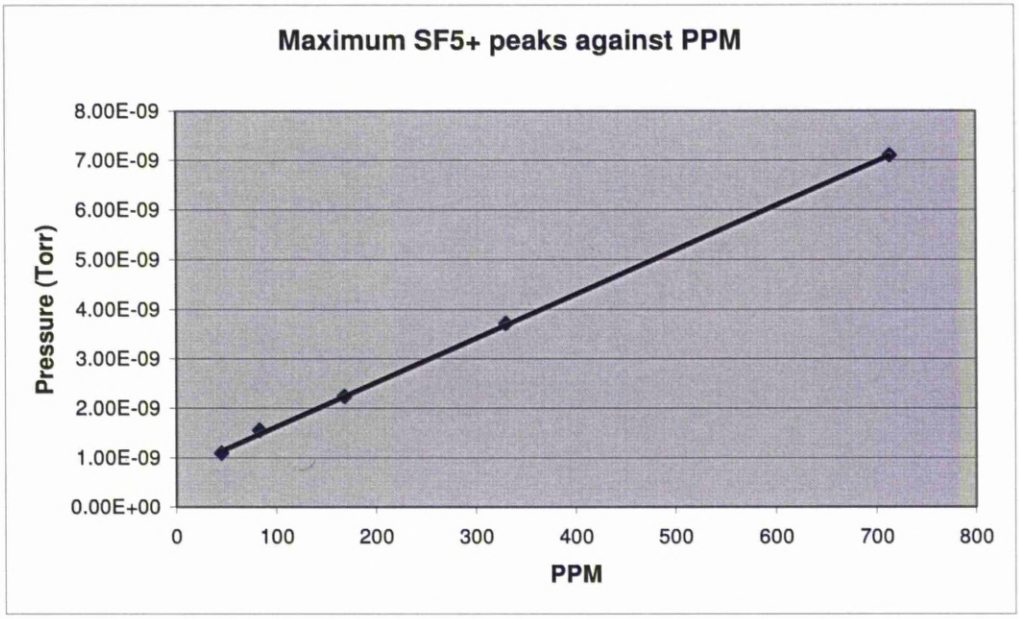


Figure 4-4: Maximum SF_5^+ peak against the concentration

A linear relationship can be seen between the SF_5^+ observed partial pressure value and the concentration in parts per million (ppm), however, measurements taken at low pressures may have uncertainties due to the peaks approaching the noise level. The ionisation peaks of SF_4^+ and SF_3^+ have also been noted and their partial pressure values have been added to that for SF_5^+. The results are shown in Figure 4-5.

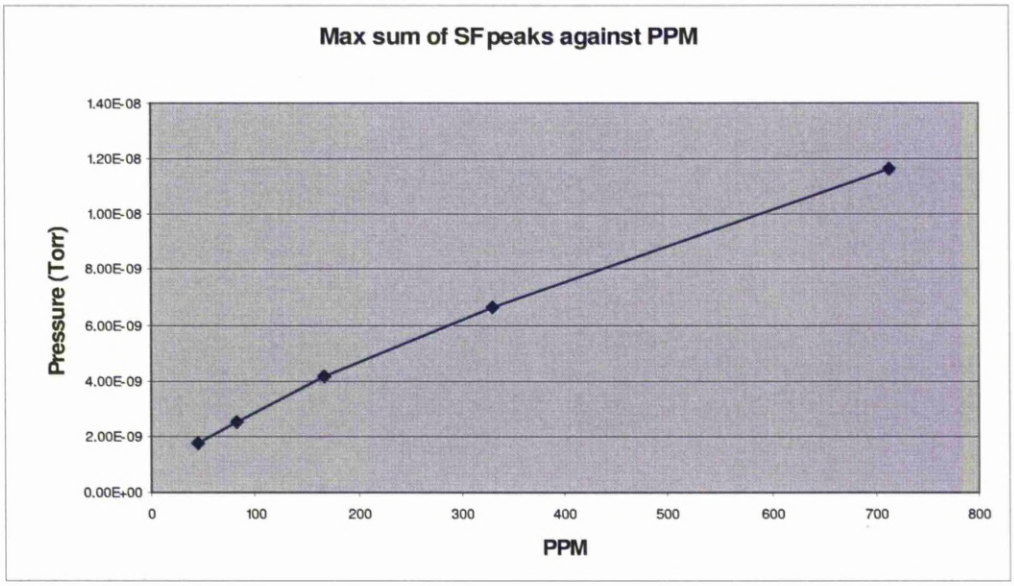


Figure 4-5: The sum of maximum SF_5^+, SF_4^+ and SF_3^+ against ppm

A near linear relationship can be seen between the sums of the maximum partial pressures for the SF_6 fragments versus the concentration. Throughout the test the N_2 peaks are also monitored. To asses whether this data is useful in the calibration process the ratios SF_5^+/N_2^+ and (Sum of SF_5^+, SF_4^+ & SF_3^+ peaks)/N_2^+ against ppm are calculated. Figure 4-6 shows a graph containing information regarding the average SF_5^+/N_2^+ versus concentration and also the average (sum of SF^+ peaks)/N_2^+ against the concentration in ppm.

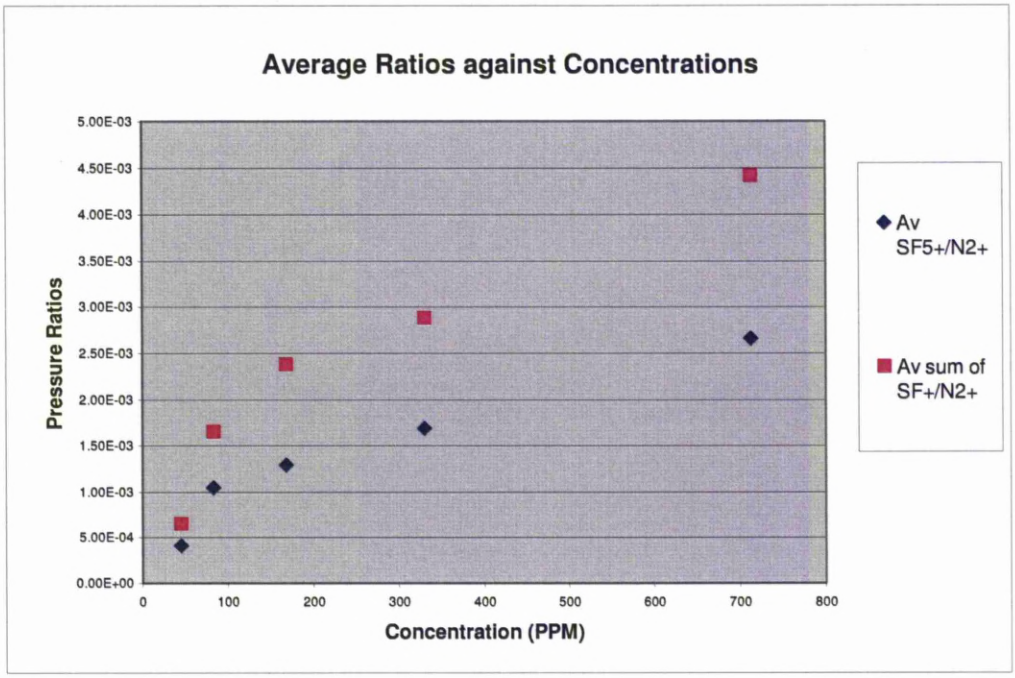


Figure 4-6: Average ratios against ppm

At higher concentrations the graph is linear but is non-linear at low concentrations. This method of calibrating a mass spectrometer would not be suitable for this reason. The scatter in the results of SF peaks is due to the transit time when taking measurements. Only the peaks have been assessed in previous discussion. The average SF_5^+ value is calculated to assess whether there is any important information to be gained. Figure 4-7 shows the averages calculated from the SF_5^+ peaks and the sums of the SF_5^+, SF_4^+ and SF_3^+ partial pressure fragments against concentration.

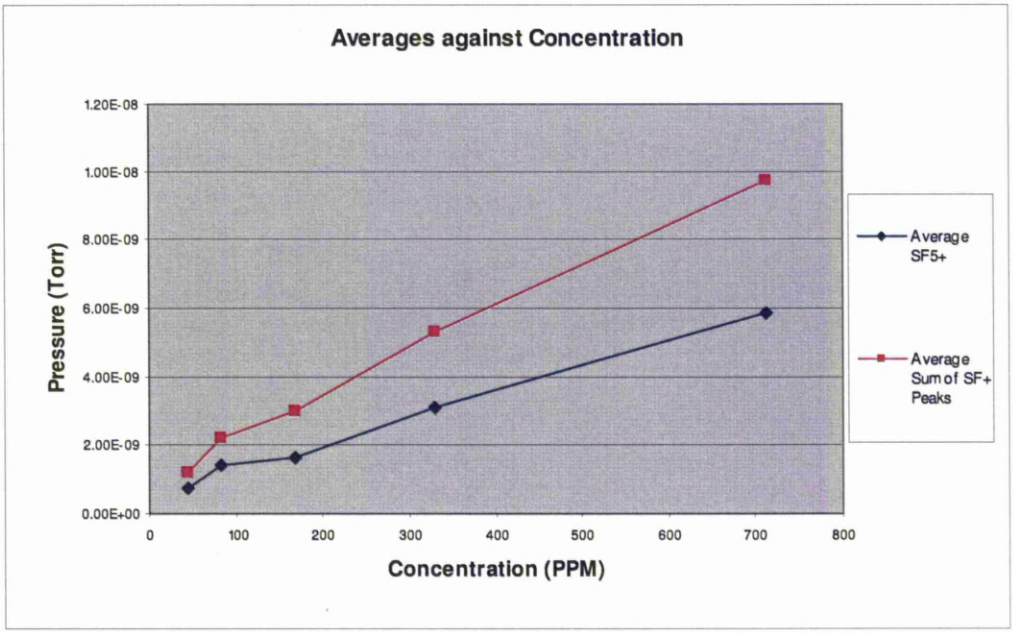


Figure 4-7: Calculated Averages against Concentration

This graph is linear above 200 ppm however towards 100 ppm the data becomes non-linear. Each of the graphs described in Figure 4-4 to Figure 4-7 show various degrees of linearity however one has better linearity than all of the others. In order that a comparison can be made Figure 4-8 shows each of the calibration results together against concentration.

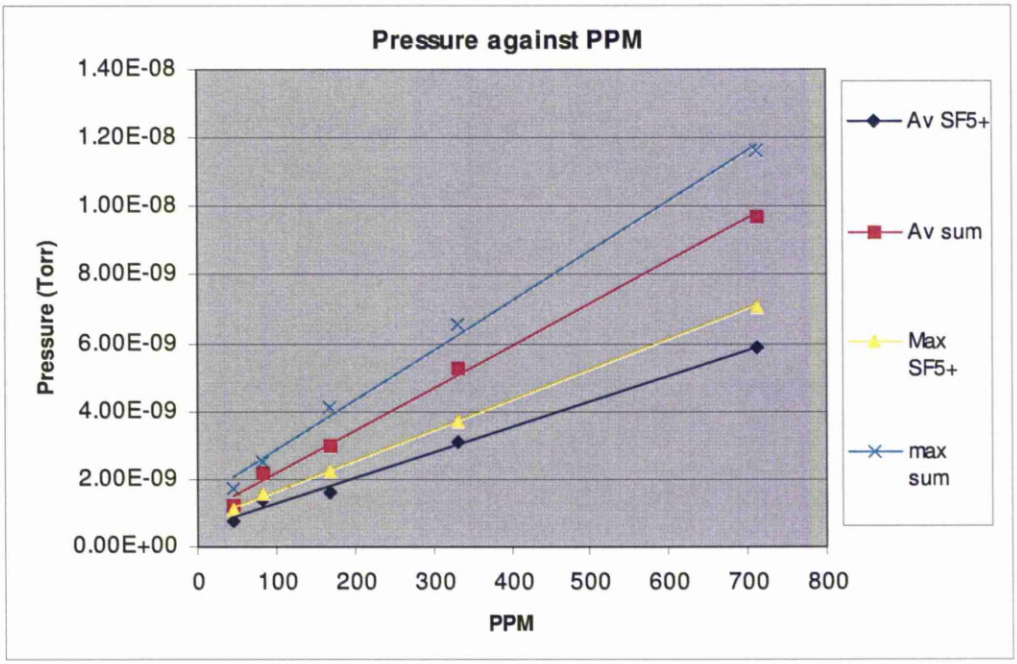


Figure 4-8: Averages and maximums against Concentrations

Trend lines have been added to show the linear relationship between the different partial pressure values and concentration in parts per million (ppm). The maximum partial pressure values are higher than the average values and have better linear characteristics due to the variability of the concentrations during the transit process. The average values at low ppm's are less linear due to the low concentrations taking longer to reach a maximum. Since the maximum partial pressure values are consistent and more linear these are suitable for calibration purposes.

A concentration value may be estimated for this system from an SF_5^+ partial pressure peak value by using the results shown in Figure 4-8. From this graph the following equation can be written;

$$Y = 9\times10^{-12}X + 7\times10^{-10} \qquad \textbf{4-1}$$

Where, Y = Pressure (mBar), X = ppm

This implies that to obtain the ppm value from an SF_5^+ partial pressure peak value, the following equation can be used (Only after these calibration results):

$$PPM = \frac{SF_5 peak - 7\times10^{-10}}{9\times10^{-12}} \qquad \textbf{4-2}$$

If the settings on the mass spectrometer were changed then a new set of calibration results would be required. It should be noted that the solid lines that appear on the graphs, are trend lines taken from excel function in the software. However these trend lines may not be suitable at lower concentrations since 45ppm was the lowest calibration sample obtainable. Any concentrations derived below this value would be based on the fact that the trend is linear and the value obtained would be an approximation.

4.3 Industry Tests

4.3.1 Vertical Exhaust Tests

Tests were conducted in order to measure leaks in an open environment. The mass spectrometer was set up to measure concentrations of leaks whose concentrations are not known.

Figure 4-9 shows the set up for tests conducted using a vertical exhaust:

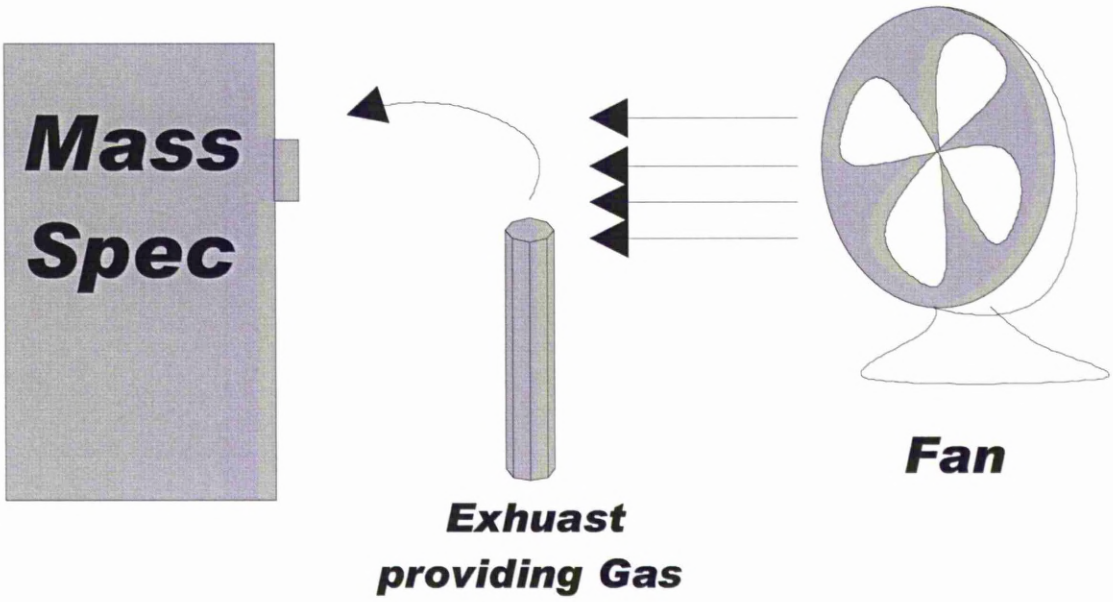


Figure 4-9: Experimental set up for B tests

4.3.1.1 Test A

The mass spectrometer nozzle was positioned 20 cm from the exhaust and a standard 240 Vac fan was placed 90 cm away on the other side. The maximum SF_5^+ partial pressure peak value noted was 1.43×10^{-9} Torr, implying an SF_6 concentration of 81 ppm.

4.3.1.2 Test B

The mass spectrometer nozzle was positioned 78 cm from the exhaust and the fan placed 90 cm away on the other side. No SF_5^+ partial pressure peak value was obtained as the concentration at this point was such that the SF_5^+ was within the noise level.

4.3.2 Evacuation of Circuit Breaker

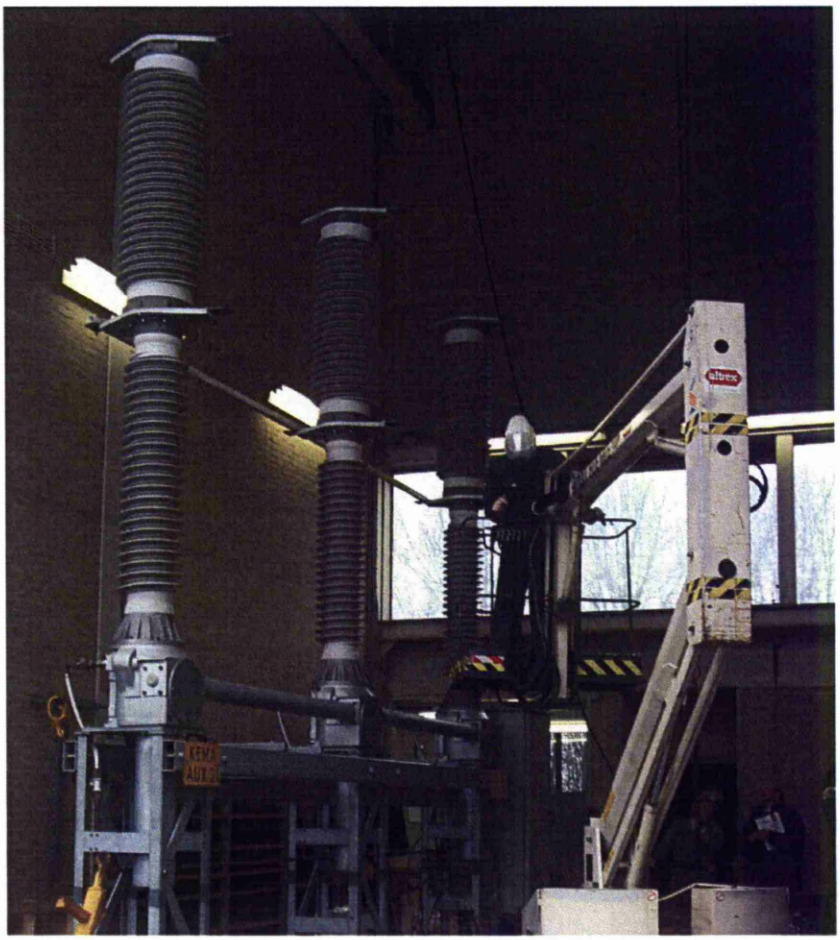


Figure 4-10: Circuit breaker evacuation

Figure 4-10 shows a circuit breaker, where the SF_6 has been evacuated and flushed with N_2 then dismantled. The mass spectrometer was used to take samples of the surrounding atmosphere as the circuit was opened. Also, when the SF_6 was removed from the circuit breaker and pumped down to vacuum, measurements were taken around a storage vessel that was used to store the removed gas. An

SF_5^+ partial pressure peak value of 7.66×10^{-10} Torr was noted, implying an SF_6 concentration of 7 ppm which is close to the background noise level.

4.3.3 Opening of circuit breaker

The pole near the driving mechanism, Figure 4-11, from the circuit breaker highlighted above was removed and placed onto the floor after the circuit breaker had been evacuated of SF_6.

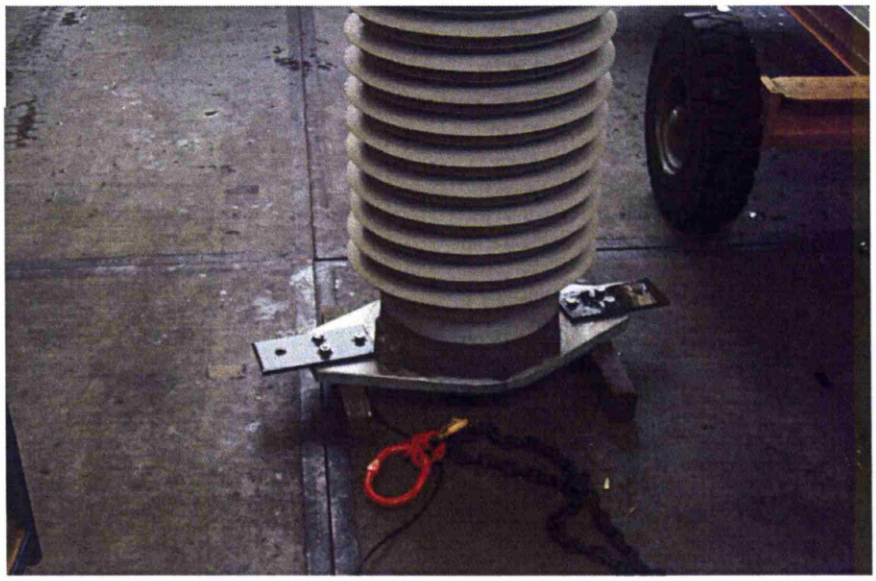


Figure 4-11: Pole near driving mechanism

Measurements were taken around the pole as it was being moved to see if any residual SF_6 could be measured. The maximum SF_5^+ partial pressure peak value that was noted was 1.55×10^{-9} Torr. This implies that there was a maximum SF_6 concentration in air at this point of 94 ppm.

4.3.4 On Site at 150 kV Gas Insulated Switchgear (GSI) Sub-Station

4.3.4.1 First Leak

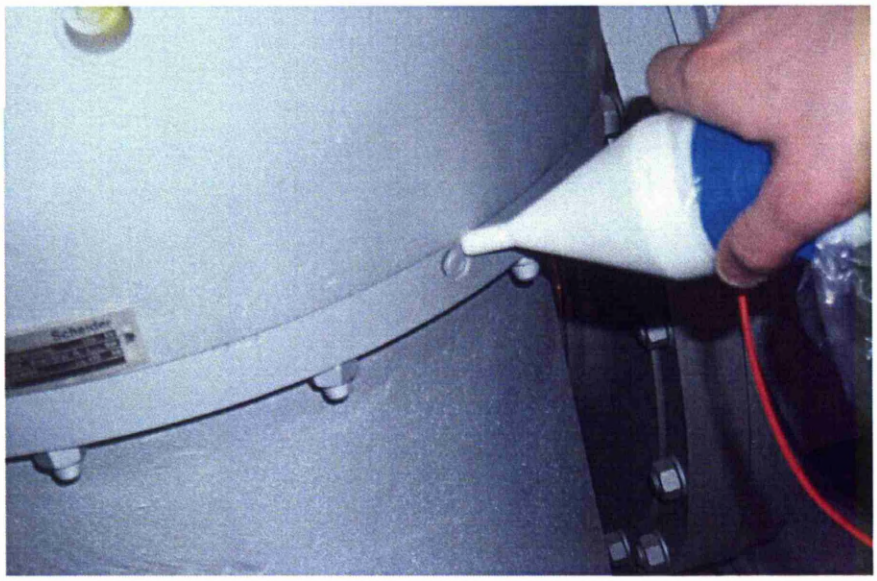


Figure 4-12: First known leak at gasket point

Samples were taken from a known leakage point, Figure 4-12. The samples were obtained using the sampling technique C described in Chapter 3 which involved filling up a sample bag at the point of measurement. The sample bag was then attached to the mass spectrometer and a number of scans were taken. The maximum SF_5^+ partial pressure peak value noted was 8.88×10^{-10} Torr. This implies that there was an SF_6 concentration of 21 ppm present in the sample taken, which, similarly to the values recorded when evacuating the circuit breaker, is close to the noise.

4.3.4.2 Second Leak

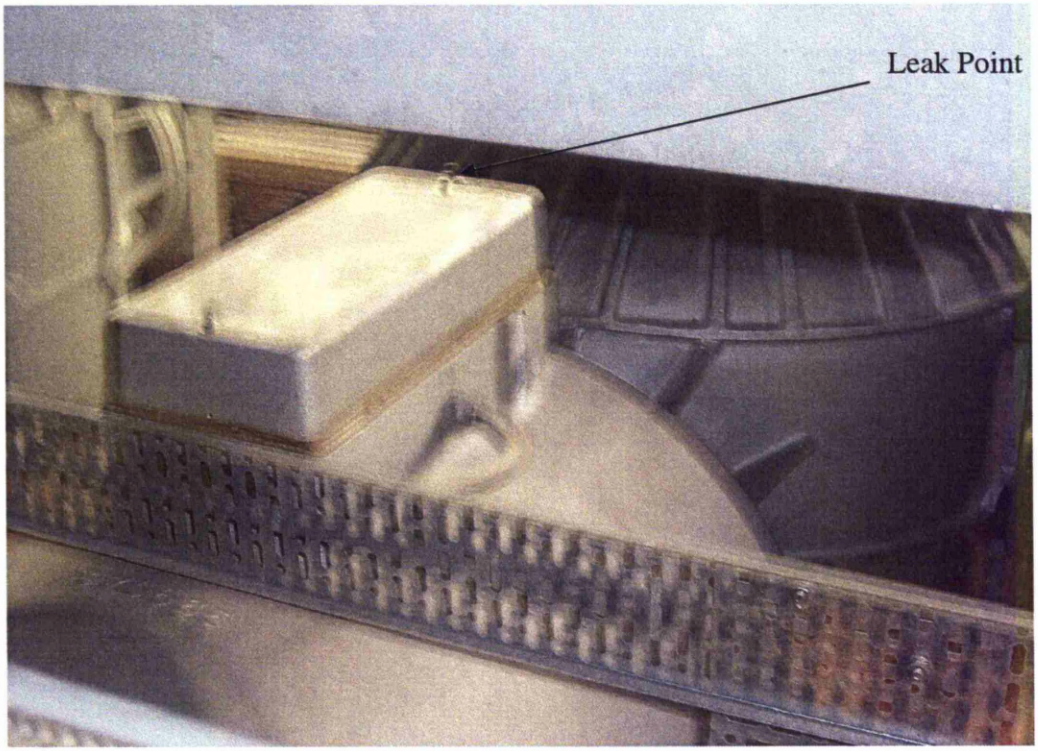


Figure 4-13: Second Leak at nut next to electrical connections

A second leak was present on the system at a nut next to an electrical panel. A sample was taken from the area around the nut using the same sampling technique as the first leak (Figure 4-13). The sample was connected to the mass spectrometer and a number of scans were taken. A maximum SF_5^+ partial pressure peak value of 1.22×10^{-9} Torr was noted. This implies that there was an SF_6 concentration of 58 ppm present in the sample taken.

4.4 CIRRUS tests

4.4.1 Introduction

A mass spectrometer was obtained that had better control over the resolution and also contained an electron multiplier. Figure 4-14 shows a typical output from the RGA300 and Figure 4-15 shows a typical output from the CIRRUS.

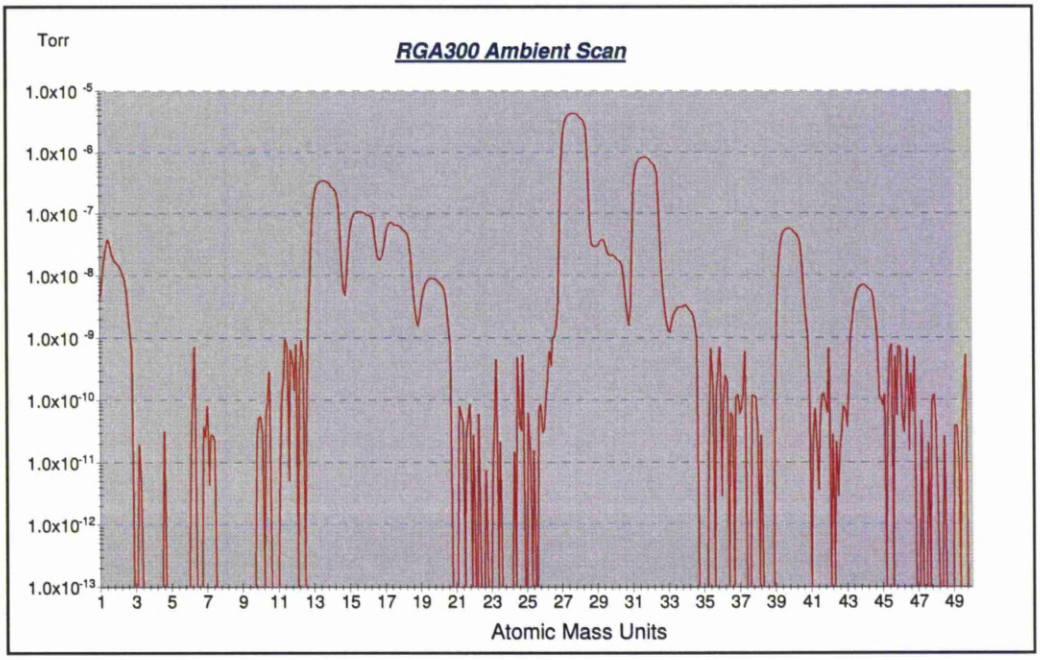


Figure 4-14:RGA300 Ambient Scan

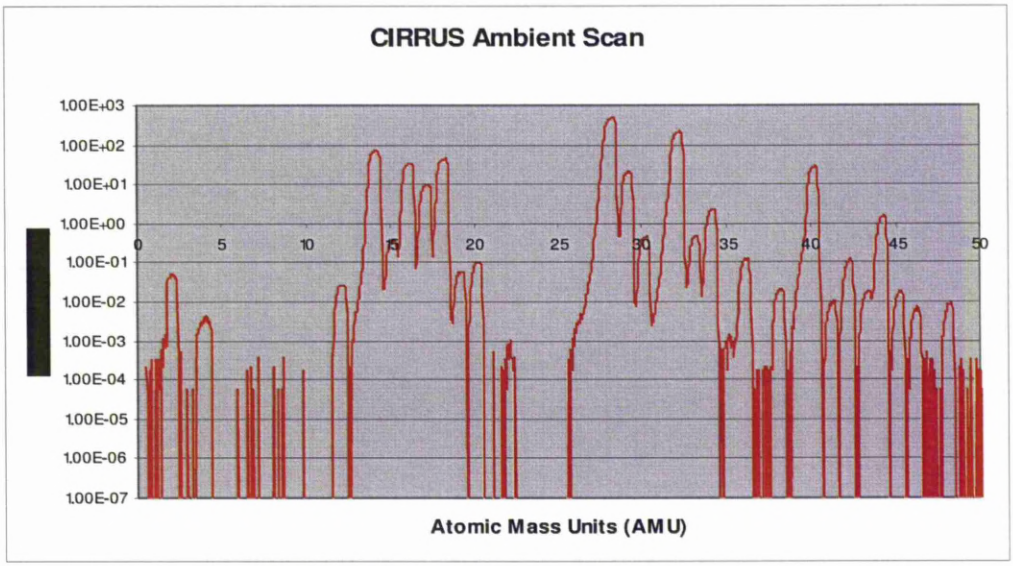


Figure 4-15: CIRRUS Ambient Scan

Unfortunately the RGA300 measures partial pressure in Torr and the CIRRUS measures partial pressure in mBar. However 1 Torr = 1.333 223 7 mBar. Using the partial pressure peak values noted at 27 AMU for each mass spectrometer a value (*SNR*) can be obtained that will give a figure that will indicate which mass spectrometer has the better signal to noise ratio:

$$SNR(dB) = 10.\log_{10}\left(\frac{P_{signal(27)}}{P_{noise}}\right) \qquad \textbf{(4-3)}$$

The RGA300 returns a value of 46 and the CIRRUS returns a value of approximately 66 implying that the CIRRUS has a better signal to noise ratio. Also the CIRRUS has a better resolution (more peaks can be resolved). This implies that lower concentrations of SF_6 may be detectable when using the CIRRUS system rather than the RGA300.

4.4.2 Calibration

Tests were undertaken to explore if it was possible to measure smaller concentrations of SF_6. The following sections give the results of a calibration of the equipment and also of tests that were performed on model systems and an SF_6 filled gas vessel. The new equipment must be calibrated in order that concentrations can be derived from the partial pressure peak values in the same manner as with the RGA300. Three concentrations for calibration were used: 20ppm, 50ppm and 200ppm. The concentrations were obtained from a gas supplier and calibration sheets for each concentration can be found in the Appendix. A graph of pressure versus concentration is constructed and can be seen in Figure 4-16.

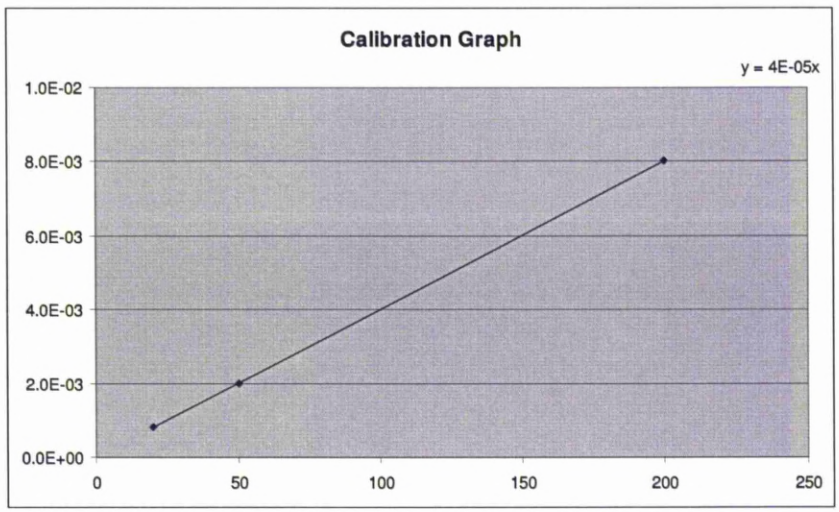


Figure 4-16: Calibration Graph for CIRRUS

The graph is a straight line as expected and the equation for the line is;

$$y = 4\times10^{-5}x \qquad \textbf{(4-4)}$$

where, y = pressure (mBar) and x = Concentration (ppm)

The lowest concentration level measurable is dependant on the noise level of the scans. Figure 4-17 shows the scans that were taken when monitoring a sample containing 200 ppm SF_6 in air. The noise level is approximately 1 x 10^{-6} mbar. This implies that the minimum ppm value measurable is 0.025 ppm or 25 parts per billion (ppb). It is not possible to obtain calibrated gas concentrations of less than 20 ppm from the gas supplier therefore it is not possible to clarify by comparison that the measurement of peak of 25 ppb is accurate but the potential is encouraging.

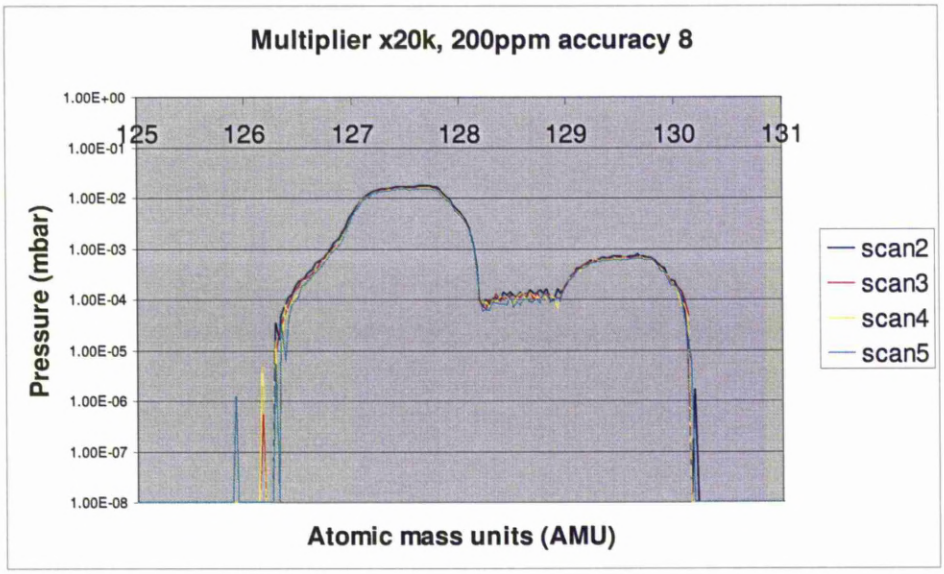


Figure 4-17: Scan measuring 200 ppm

4.4.3 Peak fall off

Tests are performed using a source that is made up of air and 200 ppm SF_6. The SF_5^+ partial pressure peak values are monitored as the source is placed at varying positions away from the RGA. The source is left to emit gas at 100, 50, 25 and 10 cm away from the RGA. It should be noted that the following tests were conducted in a stable environment where air currents were not allowed to influence results. The SF_5^+ partial pressure peak values can be seen in the following figures.

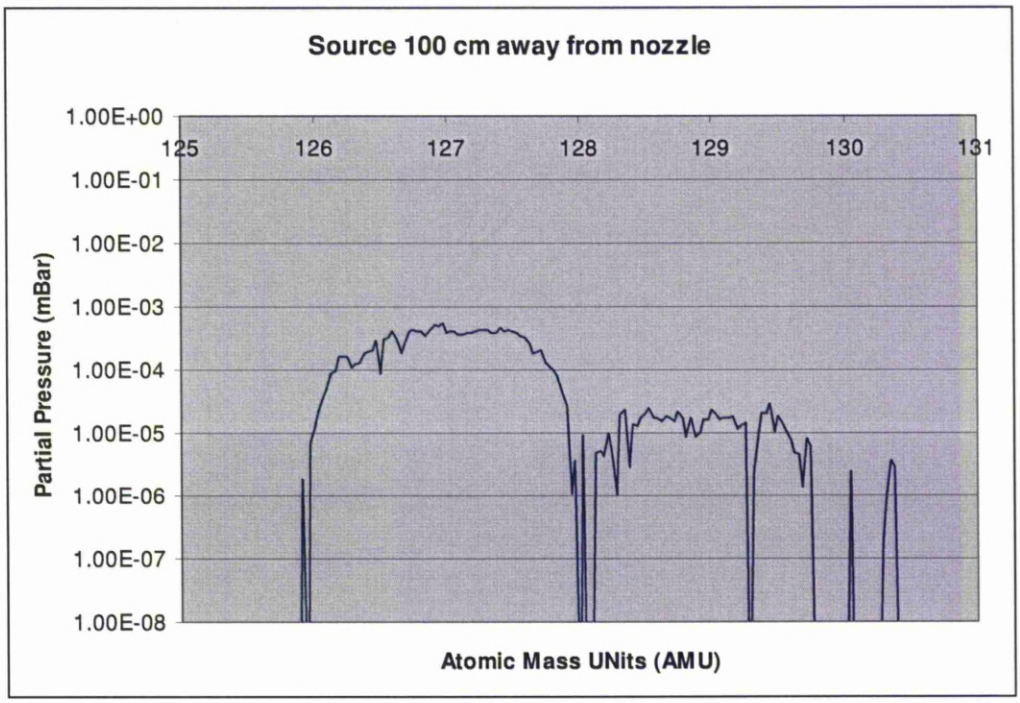


Figure 4-18: Source 100 cm away from nozzle

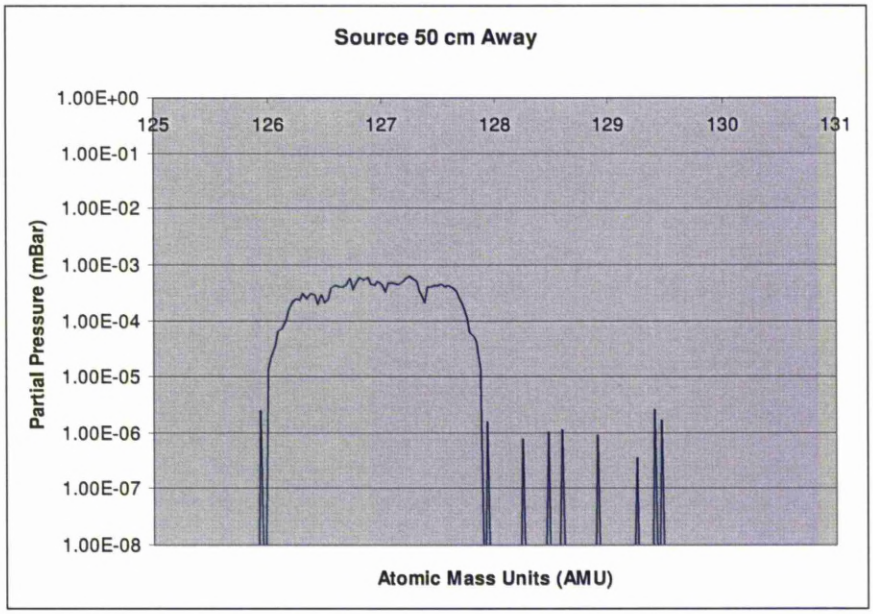


Figure 4-19: Source 50 cm away from nozzle

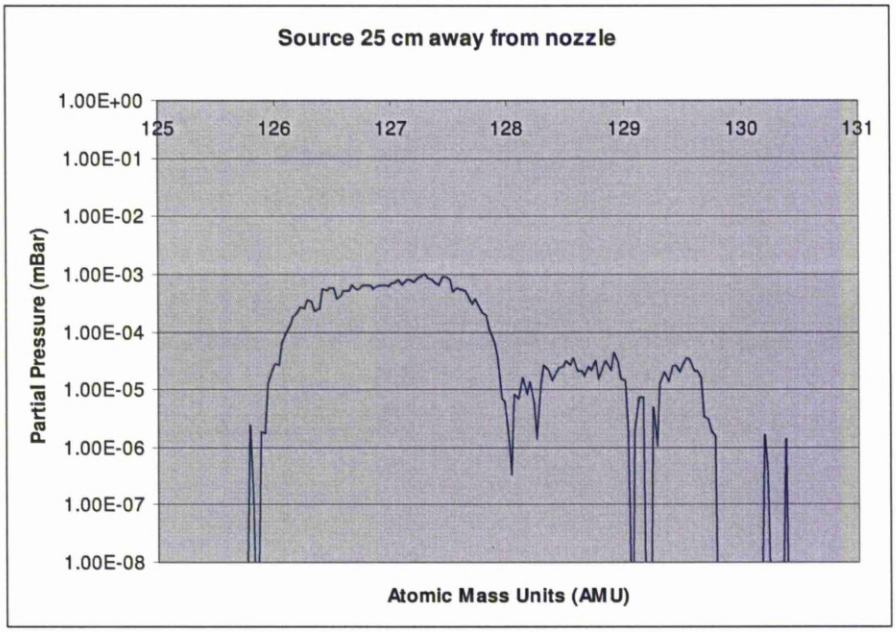


Figure 4-20: Source 25 cm away from nozzle

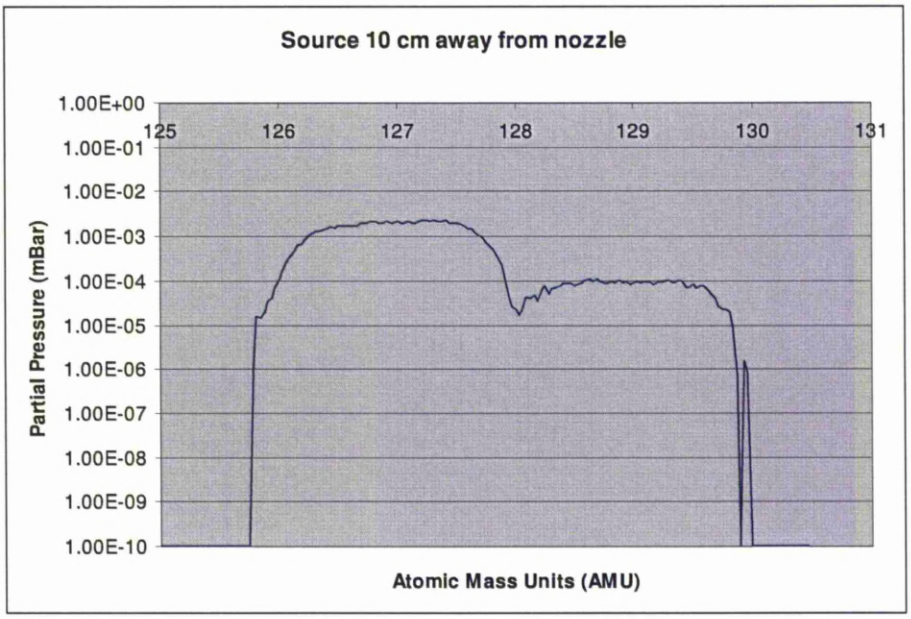


Figure 4-21: Source 10 cm away from nozzle

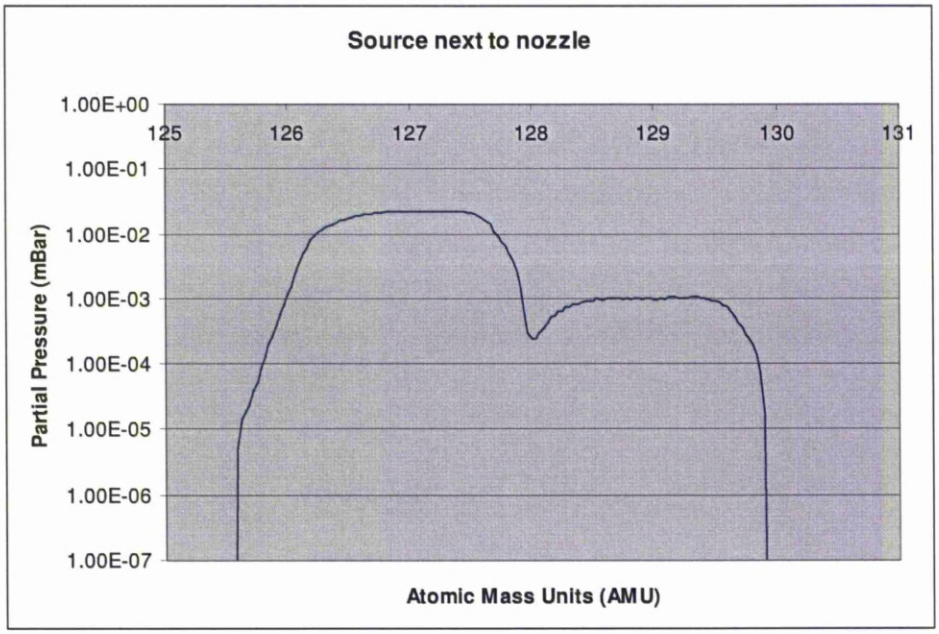


Figure 4-22: Source next to nozzle

It should be noted that two peaks can be seen. The peak at 129 AMU is due to the isotope $^{34}S^{19}F_6$. This Isotope gives a fragmented partial pressure peak at 128 AMU due to $^{34}S^{19}F_5^+$. Sulphur 34 has a natural abundance of approximately 4%. However, this second peak is only present at relatively high concentrations and therefore it is not taken into consideration when calibrating the RGA. Table 4-1 shows the $^{32}S^{19}F_5^+$ peaks with respect to the distances from the nozzle.

Distance (cm)	**Peak (mbar)**
0	$222.0x10^{-4}$
10	$22.5x10^{-4}$
25	$9.67x10^{-4}$
50	$5.91x10^{-4}$
100	$5.24x10^{-4}$

Table 4-1: Peak value versus Distance

The SF_5^+ peaks get smaller as the gas source is moved away from the measurement point. This is shown graphically in Figure 4-23. It is expected that the partial pressure peak values reduce because the gas will disperse as it reaches the measurement point.

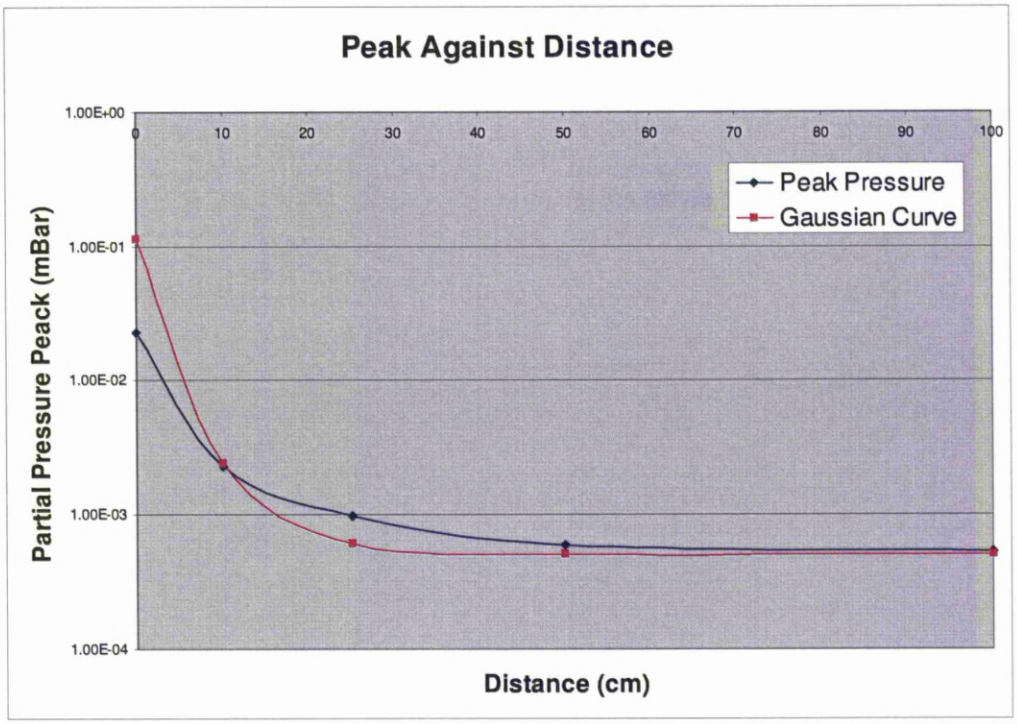


Figure 4-23: Peak versus Distance

A trend can be seen in this graph that is similar to the Gaussian model that is described chapter 2 which is highlighted. It is assumed that the minimum partial pressure peak obtainable due to noise levels is 5×10^{-4} mBar. Changes in the environment and laboratory breezes will affect the results. The reduction in SF_5^+ partial pressure peak values makes assessing the concentration at the source difficult. It is also impossible to asses how far away the source is if the concentration at the source is unknown. This means that that a different approach is required if the source concentration and position is to be obtained. A chromatic tri stimulus methodology that uses three measurement points is used proposed try

to overcome these problems. Tests are conducted on a model to assess whether this methodology is practical.

4.4.4 Two Dimensional Model Tests

4.4.4.1 Introduction

An experimental set-up to be tested for detecting gas leaks for SF_6 using a mass spectrometer with sampling tubes deployed in a tri-measurement system was set up. SF_6 is expensive and harmful for the environment therefore a substitute gas was used for assessing the performance of the system. Sampling tubes were positioned as shown in Figure 4-24.

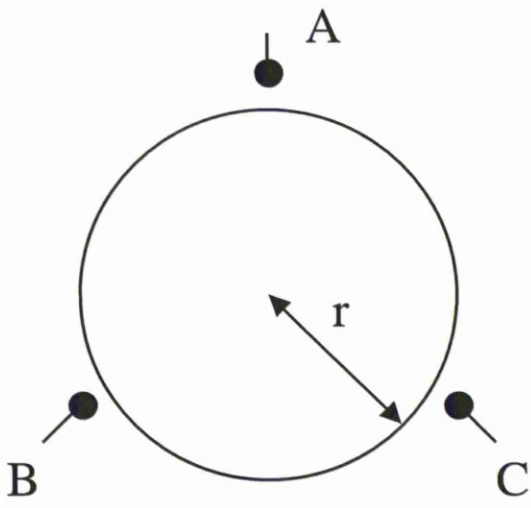


Figure 4-24: Experimental set-up

Three measurement points were set-up 120° apart from each other: A, B and C on an imaginary circle of radius 38 cm. Mass Spectrometer scans were taken at each of the points under test conditions. Experimental test leaks were simulated inside the imaginary circle at different points using Helium and CO_2.

4.4.4.2 Helium tests

The following measurements were taken from measurement point "A" only. Helium was released at the centre of the circle (log 3), then half way from the centre to the point A (log 4) and then next to point A (log 2), Figure 4-25.

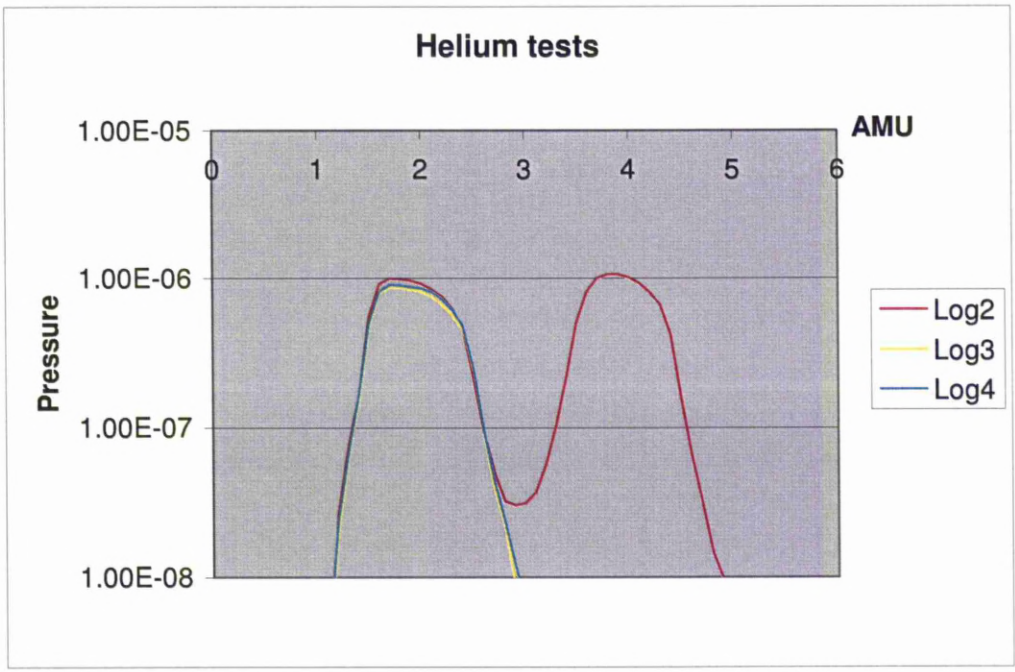


Figure 4-25: AMU scan of Helium measurements

Helium is mass 4 and it can be seen from the AMU peaks that only log 2 picked up any Helium, this is when the source was next to the measurement point. This gas is therefore not suitable for testing a leak detection system as it cannot be detected even over a small range. Helium is a very light gas and the gas rises into the atmosphere before it reaches the measurement point, Figure 4-26.

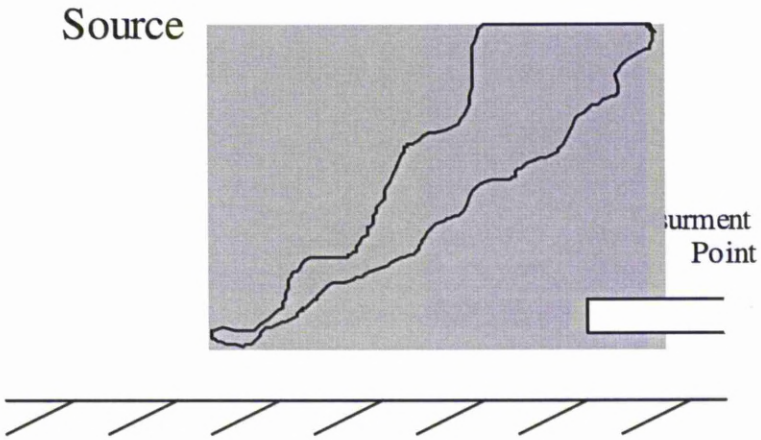


Figure 4-26: Helium test

4.4.4.3 CO2 tests

Helium was replaced by CO_2 as the source gas and the tests were repeated. The CO_2 was placed at the following points in the circle, Figure 4-27.

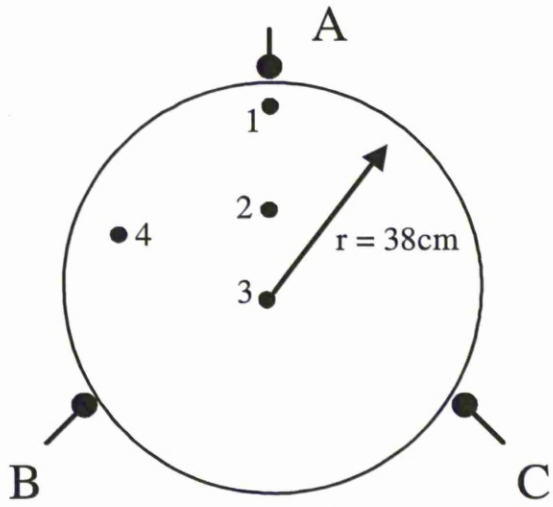


Figure 4-27: Source points

The leak was initiated and the mass spectrometer was set to start logging, concentrating around 44 AMU. This partial pressure peak is one of the fragmentation peaks of CO_2. CO_2 has fragmentation peaks at 12, 16, 28, 44, 45 and 46, however 44 is chosen as the peak to be monitored because it is more removed from the other atmospheric gases present in the air with lower AMU values. The leak was stopped after 50 seconds and the mass spectrometer was left to scan for a further 2 minutes and 20 seconds to monitor the dissipation of the gas. Figure 4-28 to Figure 4-31show the partial pressure peak value at 44 AMU against the scan number that was observed at each measurement point following the tests described above.

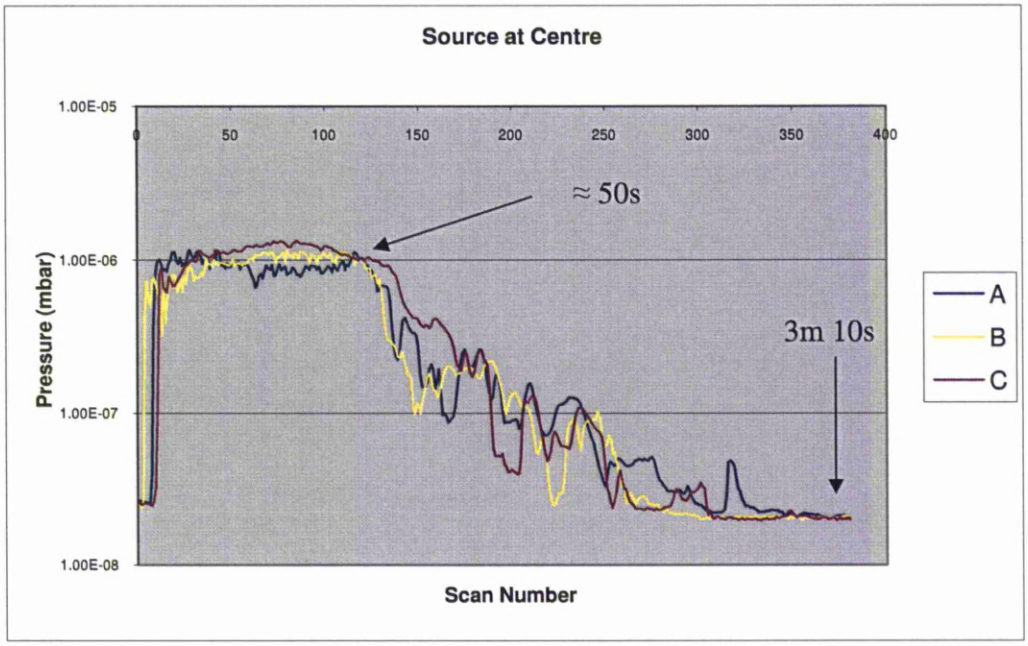


Figure 4-28: Source at Centre

This figure shows a rapid response of the partial pressure at 44 AMU when the gas is introduced. The partial pressure value is constant for a specific period and then it decays when the gas is switched off back to the background level. The time axis on the figure is expressed as scan number but is indicative of time.

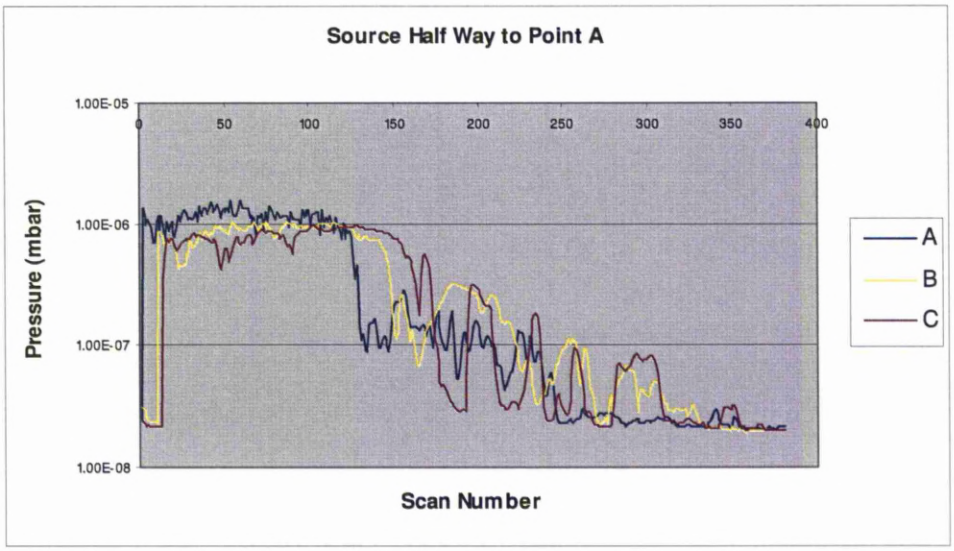


Figure 4-29: Source half way to A

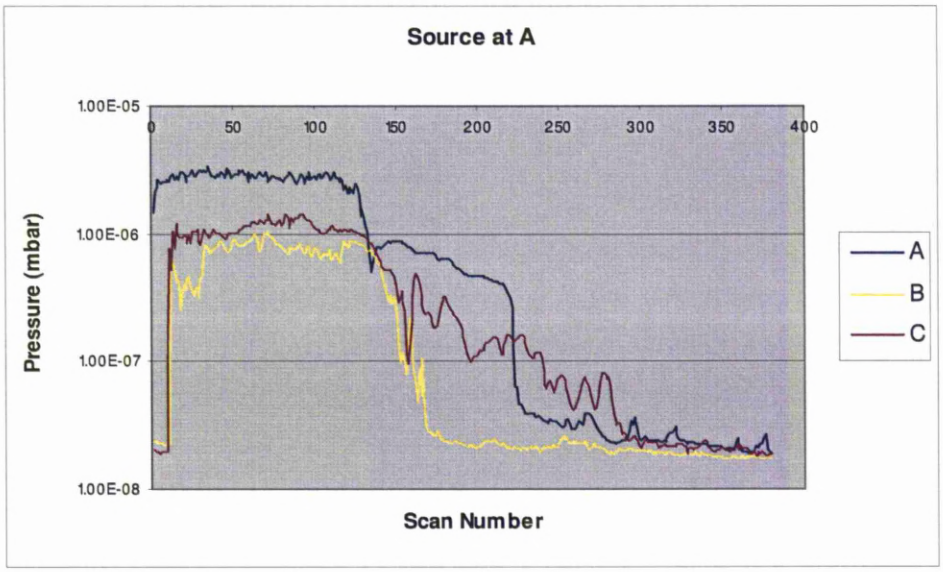


Figure 4-30: Source at A

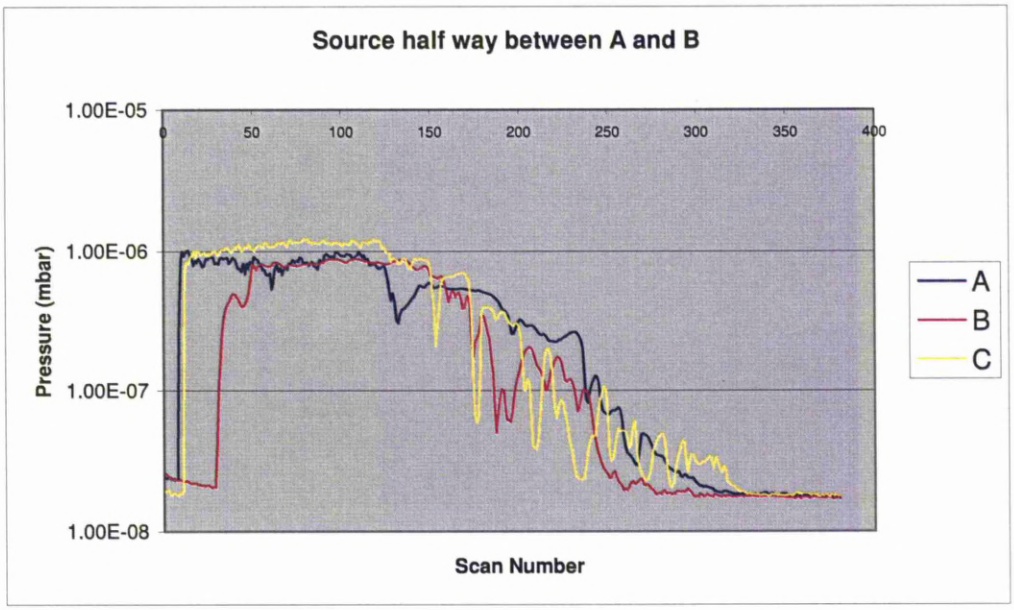


Figure 4-31: Source half way between A and B

The blue line represents the scan taken at point A, the yellow line represents the scan taken at point B and the red line represents the scan taken at point C. It can be seen that for each different source point the measurements taken at A, B and C vary.

Figure 4-30 shows the data taken when the source place next to A. A larger partial pressure can be seen at measurement point A. This is because the closer the source is to a measurement point then the higher the concentration due to less dispersion and hence the higher partial pressure peak value. The time response is also related to distance between the leak and the measurement point. Examination

of Figure 4-31, which is the scan taken when the source is half way between point A and point B shows that the scan taken from point C has a longer transit time than the other two and also when the source is at the centre that transit times and partial pressure peaks all have similar values.

4.4.5 Gas Vessel Leak Detection

Following the model tests using CO_2, a small vessel (see Figure 2-2 in chapter 2) is filled with SF_6. However, since a new mass spectrometer (CIRRUS) is now being used then a new set of calibration measurements are required so that the concentration of SF_6 in air can be identified at each of the measurement points that make up the three dimensional model, Figure 4-32.

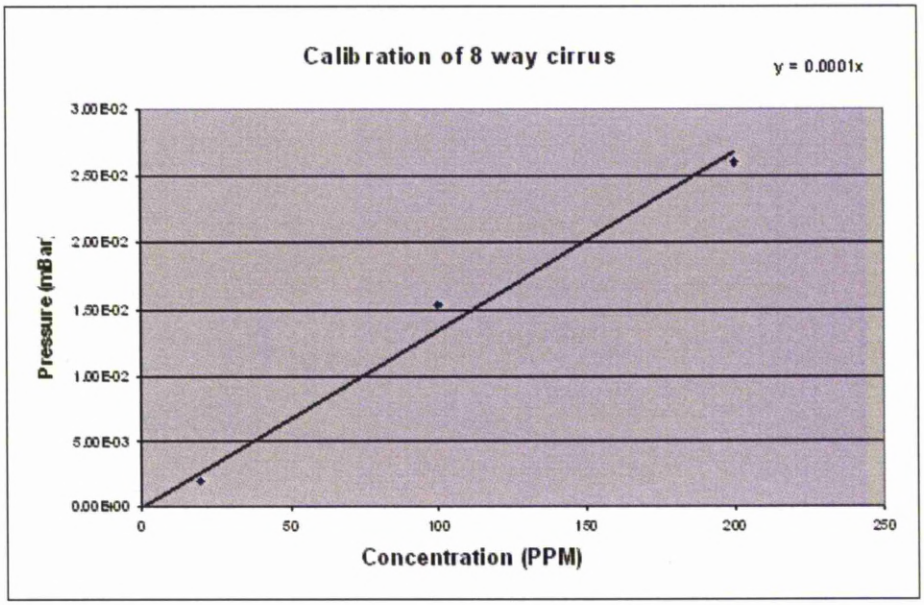


Figure 4-32: Calibration of Cirrus with Valve attached

From the trend line in the above figure the following equation is obtained:

$$y = 1.25 \times 10^{-4} x$$

where,

x = Concentration (ppm) y = Partial Pressure

To simplify; the concentration of SF_6 in air measured in ppm is obtained by multiplying the pressure measured in mBar by 10,000. However, this is an approximate value as only three measurement points have been used.

The tri measurement system is setup around the vessel as shown in Figure 4-33. The Vessel is known to have a leak since the pressure drops when it is filled with gas. However, the position of the leak is unknown.

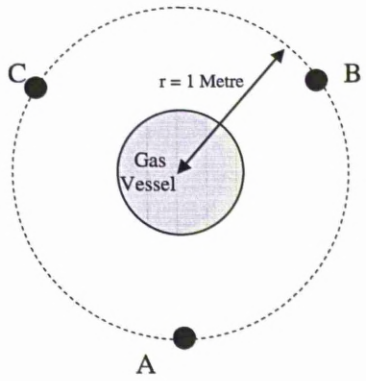


Figure 4-33: Tri Stimulus layout

Scans were taken at points A, B and C to monitor for SF_6 by recording the partial pressure value at mass 127 which corresponds to the SF_5^+ fragmented peak.

The scans taken can be seen in Figure 4-34. Each 1 scan takes 1 minute and 20 seconds and it can be seen that it takes 8 minutes for any SF_6 to reach the mass spectrometer.

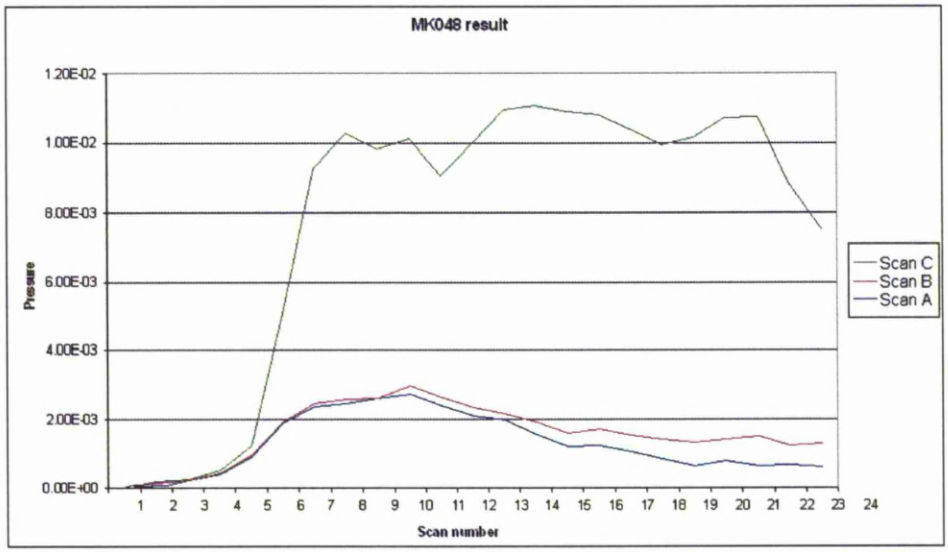


Figure 4-34: Leak Check Scans for AMU 127

It can be seen that Scan C has a much higher peak then the other two scans and therefore it is expected that the leak is closest to measurement point C and has a peak of 1 x 10^{-2} mBar which implies that there is a concentration of 100 ppm SF_6 in air at that point; however as with the CO_2 tests the location and concentration at the source of the leak cannot be identified from this data. This data is analysed further in order to obtain more useful information in chapter 5.

4.4.6 Three dimensional model tests

4.4.6.1 Introduction

After samples are successfully taken using the two dimensional setup around a gas vessel, the next step is to set up a three dimensional space in order that a three dimensional profile can be built up. The following measurement points are used with sample points placed in vertical and horizontal planes, Figure 4-35.

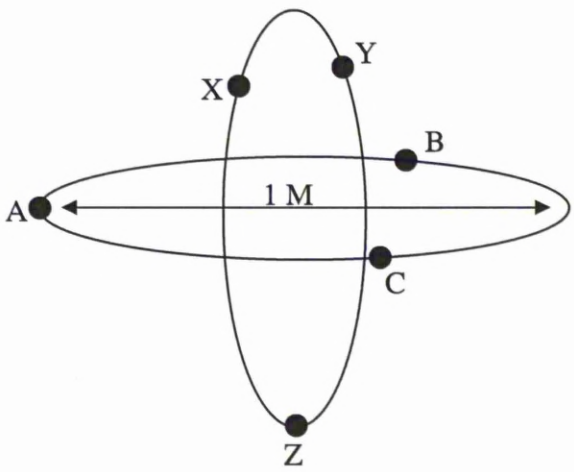


Figure 4-35: 3 Dimensional Measurement points

The measurement points A, B & C are associated with the horizontal plane and the measurement point X, Y & Z are for the vertical plane. The following sections describe the different tests that were performed using this configuration.

4.4.6.2 Leak next to one measurement point at 200 ppm

An SF_6 leak of 200 ppm was positioned next to measurement point Y on the inside of the tri measurement setup. The CIRRUS was used in conjunction with the 8 way valve and the electron multiplier was used. Equal length tubes were connected to six of the valves and the remaining two were disabled. A recipe is written in the Cirrus' software to instruct the Cirrus to take one scan between 123.5 AMU and 129.5 AMU at each of the measurement points. Figure 4-36 to Figure 4-41 show the resulting scans. These figures show the partial pressure values in mBar against Atomic Mass Unit (AMU). It can be seen that only point Y has a detectable response.

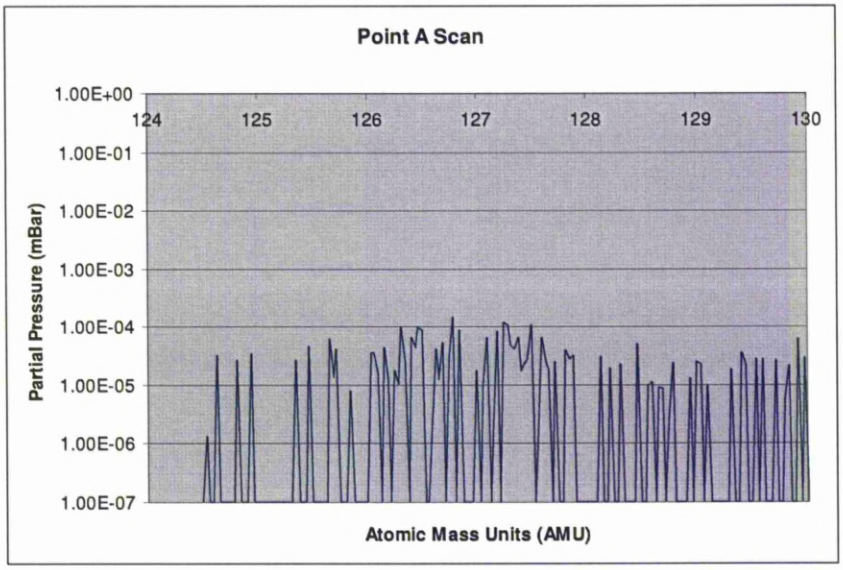


Figure 4-36: Scan taken at Point A

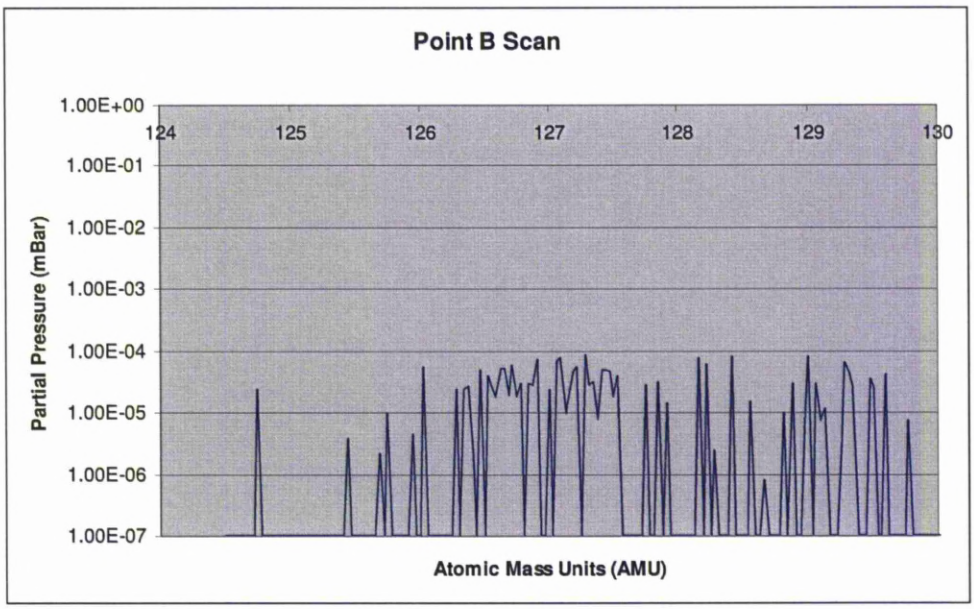


Figure 4-37 Scan taken at Point B

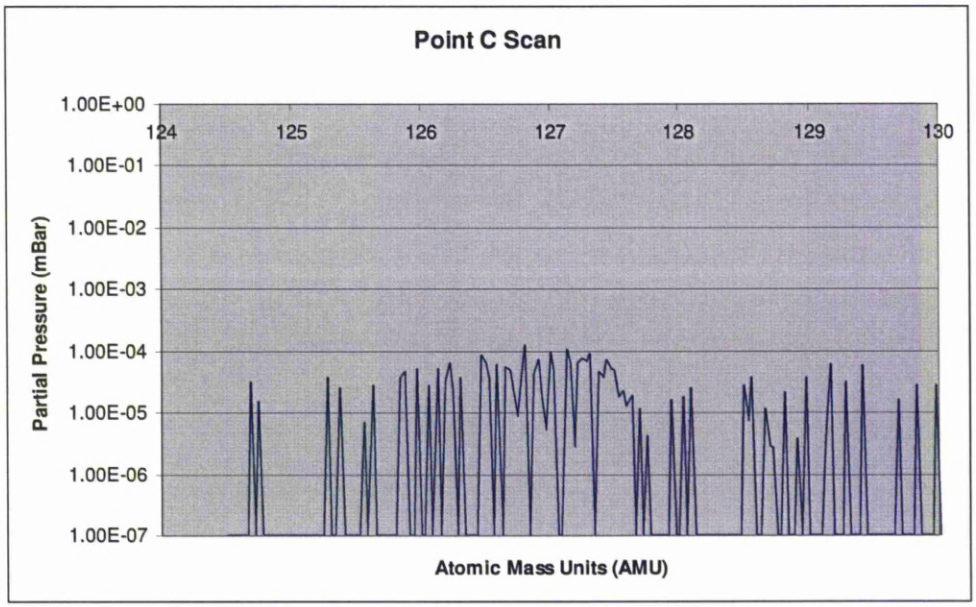


Figure 4-38: Scan taken at Point C

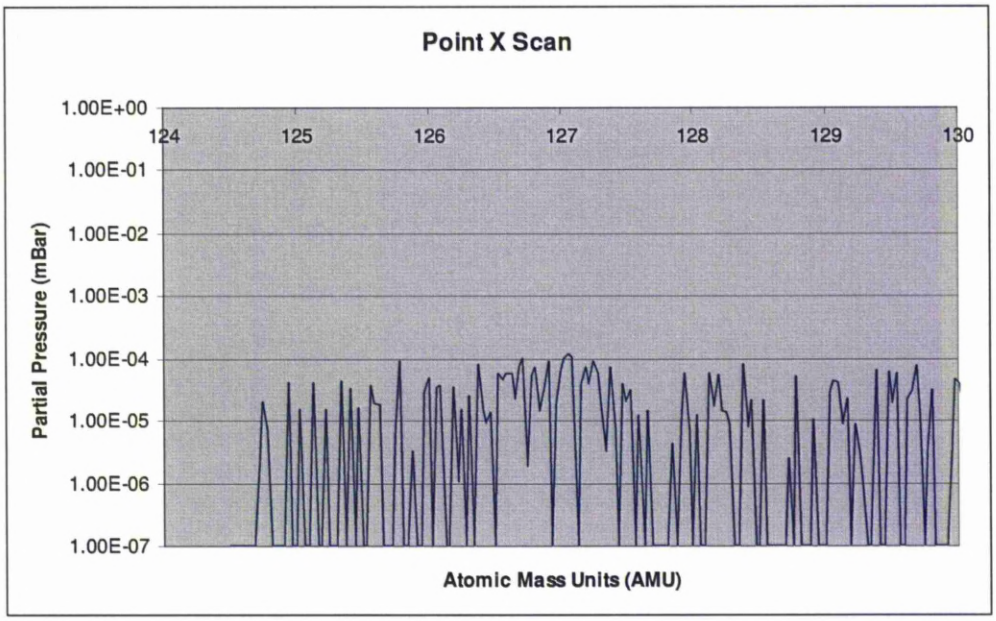


Figure 4-39: Scan taken at Point X

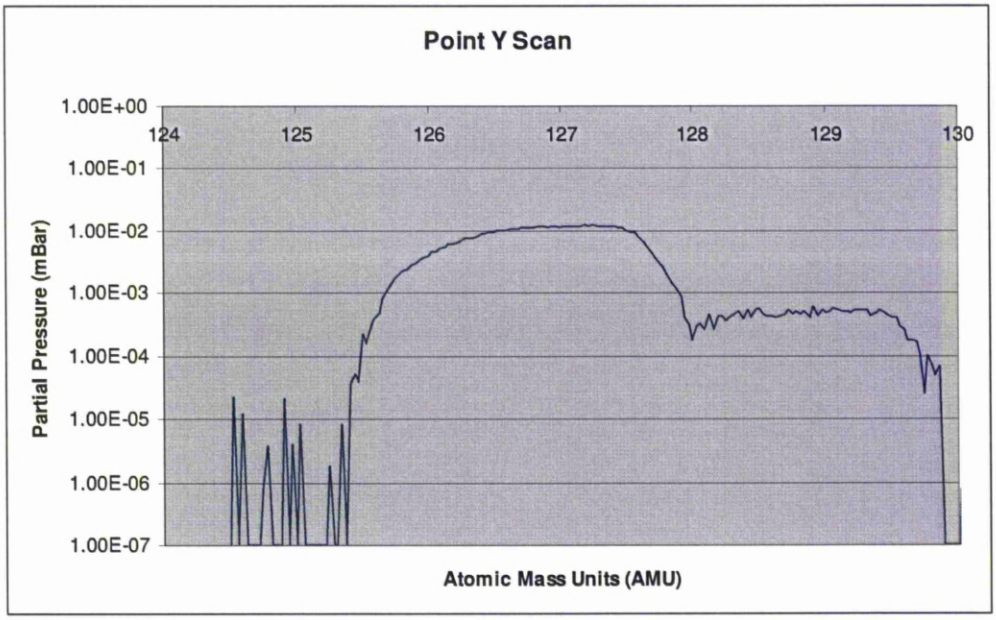


Figure 4-40: Scan taken at Point Y

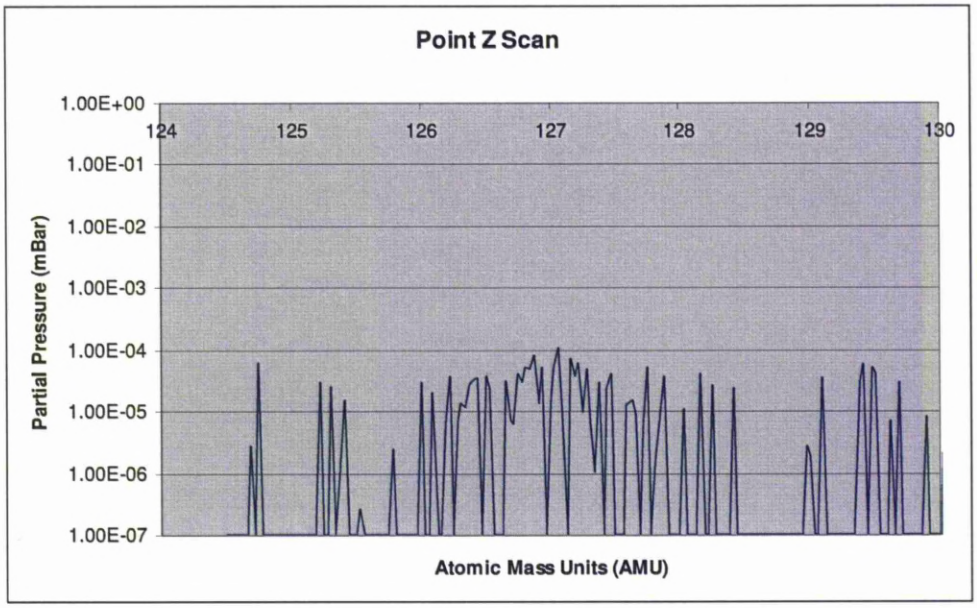


Figure 4-41: Scan taken at Point Z

No distinctive peaks can be seen on the scans representing the data that was collected at points A, B, C, X & Y. However within the data there are suggestions that that there seems to be some trend around Atomic Mass 127 indicating that there may be a small peak buried in the noise of the mass spectrometer scans. There is a very positive SF_5^+ peak at point Y as would be expected since the leak was placed right next to the measurement point. From calibration (Figure 4-32) it can be seen that the partial pressure peak value measured at point Y indicates a concentration in the order of 200 ppm as expected. This data will be further analysed in Chapter 5. The results also indicate that gas samples are unaffected by traveling along the tube to the Mass Spectrometer.

4.4.6.3 Leak Placed Close to the Centre of 3 Dimensional Space

A leak of 200 ppm was placed in the centre of the two dimensional space and a scan was taken at each measurement point between 125 AMU and 129 AMU to see if the SF_6 can be detected. The following figures show the scans that were obtained from the six measurement points. The ABC scans represent the horizontal plane and the XYZ scans represent the vertical plane.

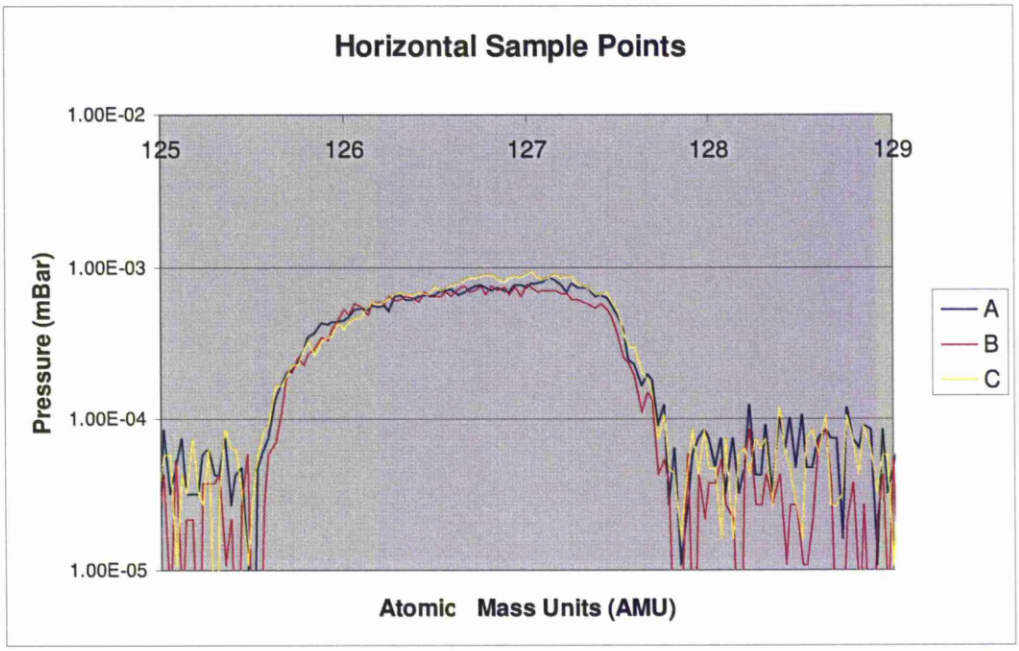


Figure 4-42: ABC Plane of 200 ppm in centre of 2D Space

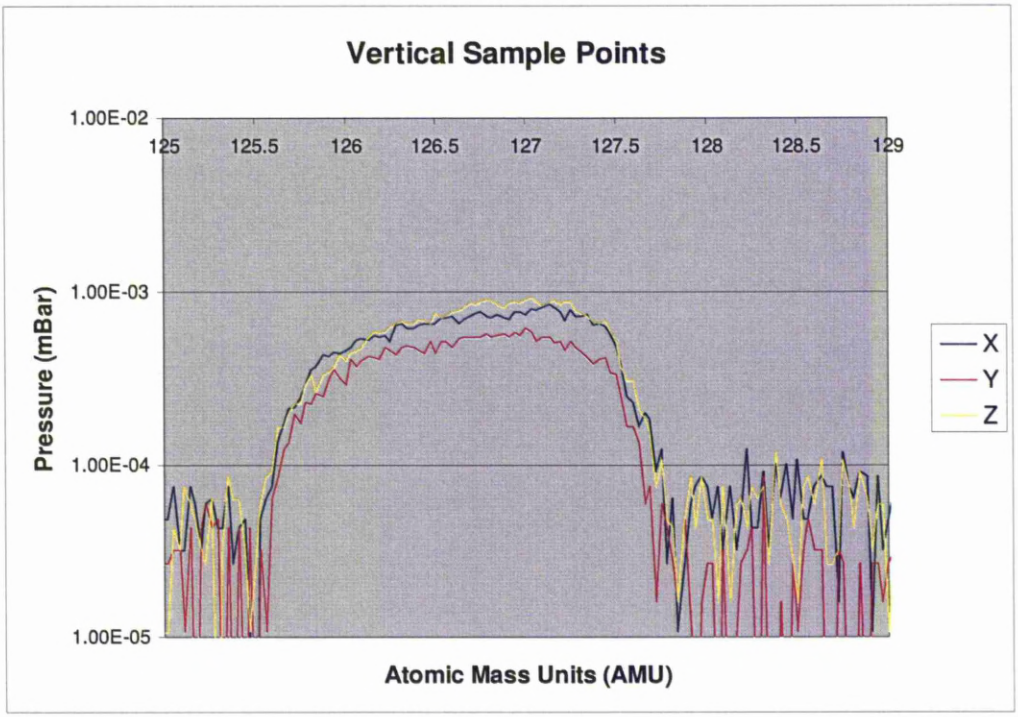


Figure 4-43: XYZ plane of 200 ppm in centre of 2D Space

It can be seen that the partial pressure peaks measured at each measurement point is similar which is a good indication that the leak is somewhere close to the centre of the 2D space as expected. From calibration the scans indicate that a concentration of approximately 10 ppm is being detected at the measurement points. The noise level in these scans is at a pressure of approximately 1 x 10^{-4} mBar which equates to 1 ppm.

4.4.6.4 Leak situated in the bottom half of 3-Dimensional Space

A leak of concentration 100 ppm SF_6 in air was placed in the bottom half of the three dimensional system and allowed to migrate into the space. The CIRRUS was set to record 60 scans over three hours between 118 and 136 AMU. Ten scans were recorded at each measurement point and each scan contained 672 measurements, Table 4-2 :

Points	Scans									
A	1	7	13	19	25	31	37	43	49	55
B	2	8	14	20	26	32	38	44	50	56
C	3	9	15	21	27	33	39	45	51	57
X	4	10	16	22	28	34	40	46	52	58
Y	5	11	17	23	29	35	41	47	53	59
Z	6	12	18	24	30	36	42	48	54	60

Table 4-2: Scans for each measurement Point

Taking Scan 1 at Point A, Figure 4-44, it can be seen that it is possible to distinguish a signal buried in the noise in the region of 127 AMU.

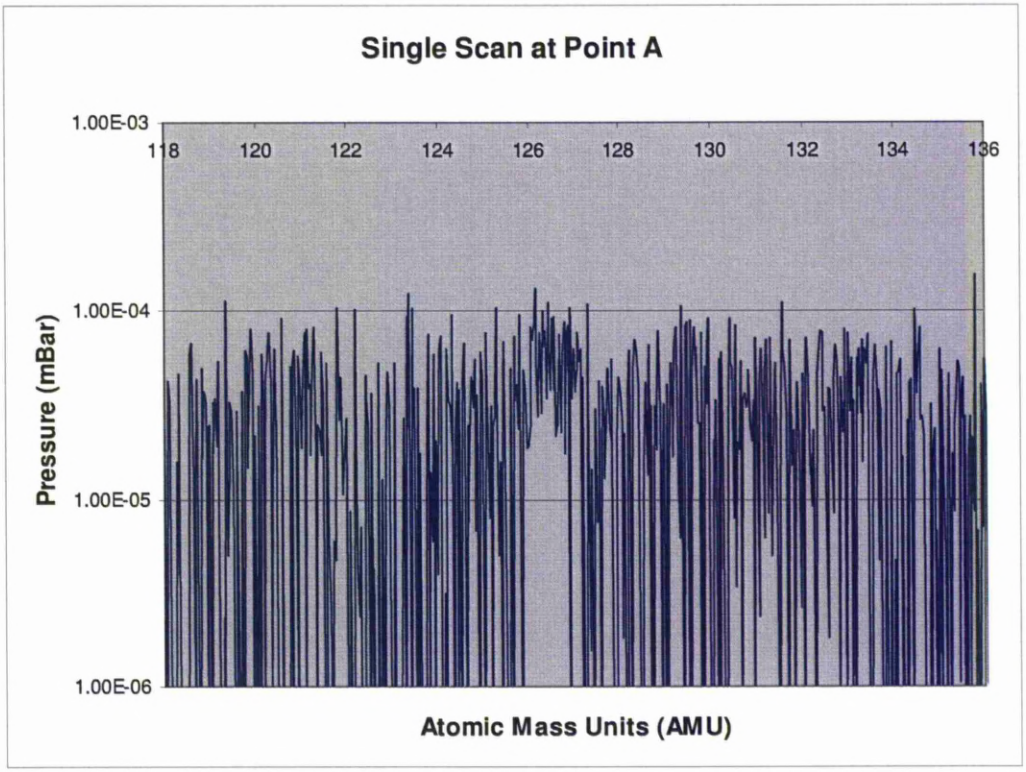


Figure 4-44: Point A, Scan 1 at 100 ppm

To reduce the effects due to noise, an average was taken of the 10 scans at each point. The figures below show the resulting averages at each point:

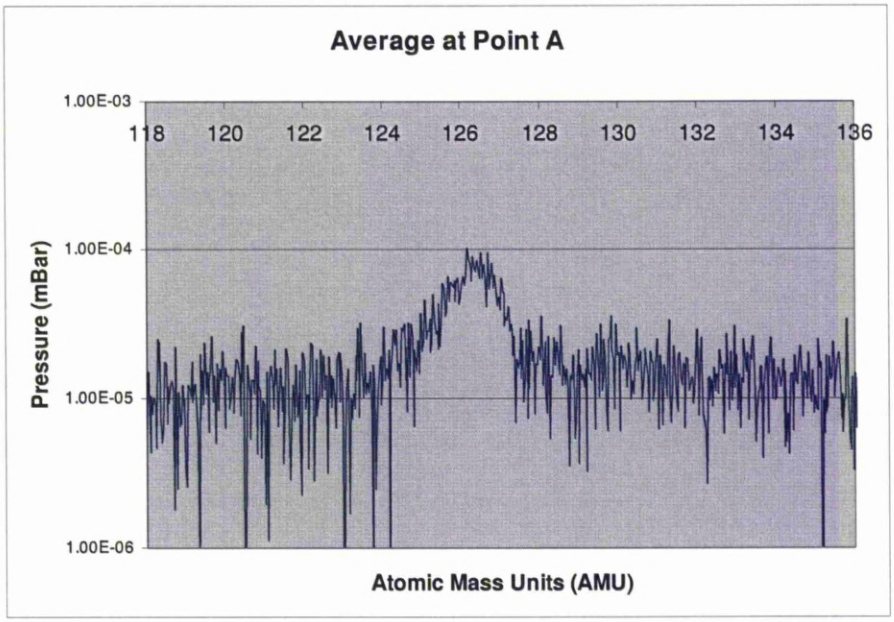


Figure 4-45: Average at Point A at 100 ppm

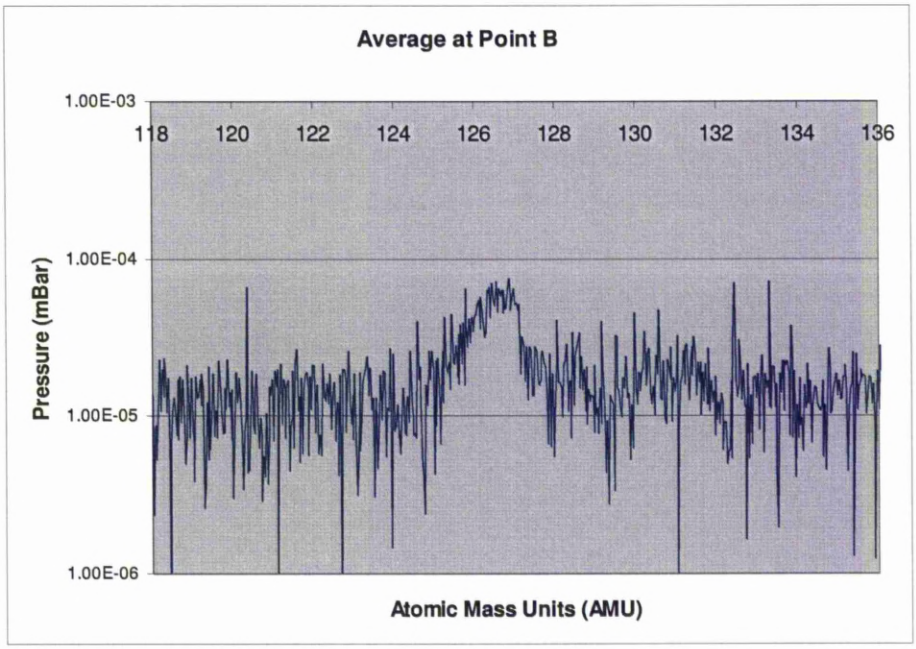


Figure 4-46: Average at Point B at 100 ppm

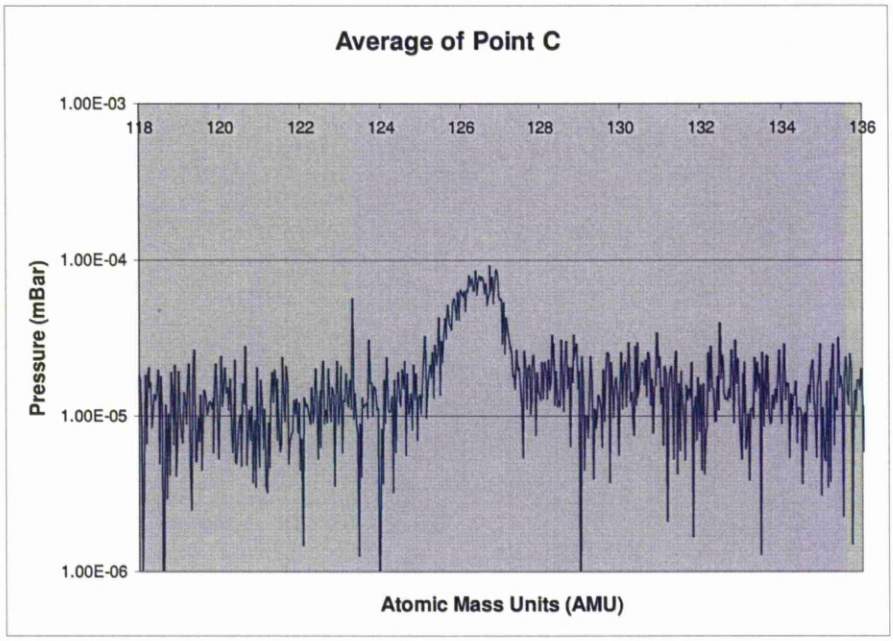


Figure 4-47: Average at Point C at 100 ppm

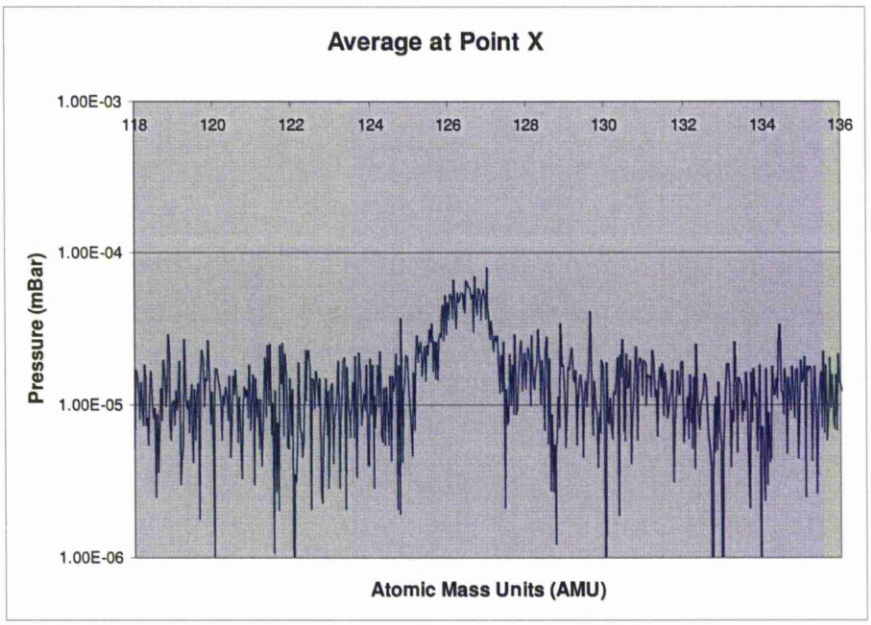


Figure 4-48: Average at Point X at 100 ppm

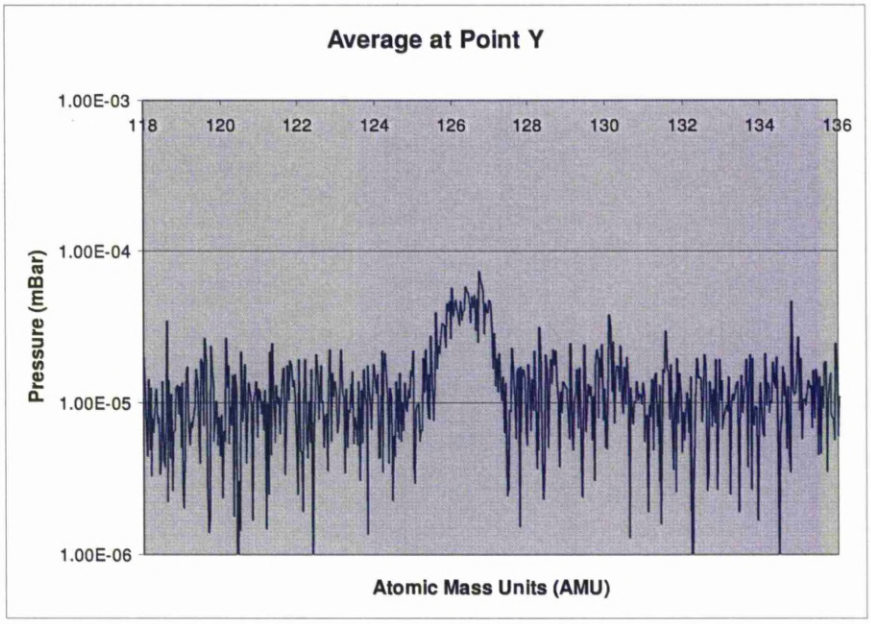


Figure 4-49: Average at Point Y at 100 ppm

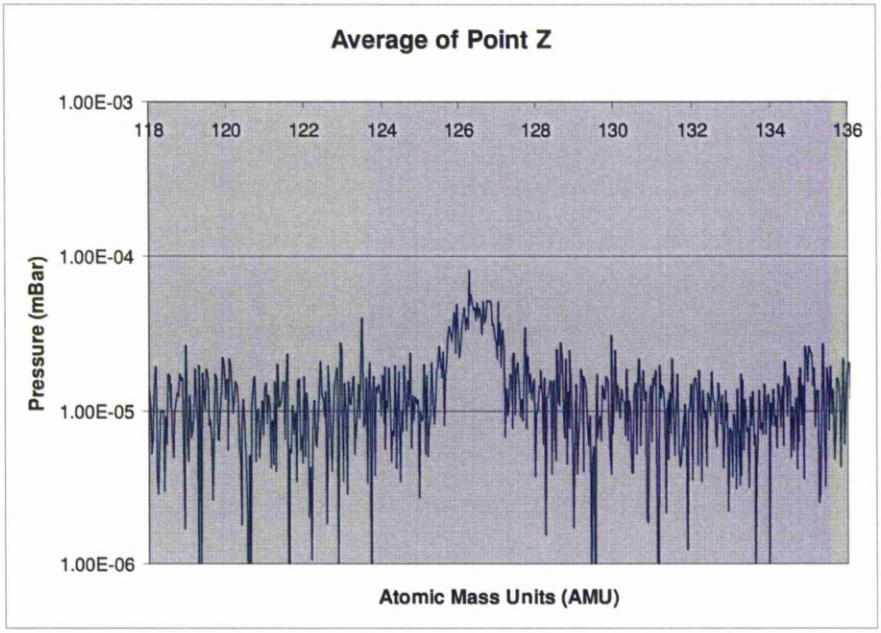


Figure 4-50: Average at Point Z at 100 ppm

The SF_5^+ partial pressure peak value can be seen much more clearly at each measurement point and the noise level has dropped to $1x10^{-5}$ mBar which equates to 100 parts per Billion (ppb). It is estimated that the SF_5^+ peaks are in the order of 1 ppm.

4.4.6.5 Low concentration at centre of 3 Dimensional Space

A leak of a concentration of 20 ppm SF_6 in air was located inside the three dimensional space to explore if a relatively small amount of SF_6 could be detected. The leak was allowed to fill the space and the mass spectrometer was set to take 10 measurements from each of the six points, a total of 60 scans were obtained between 125 AMU and 129 AMU. Examining the first scan at measurement Point A, (Figure 4-51) it can be seen that the data is quite random.

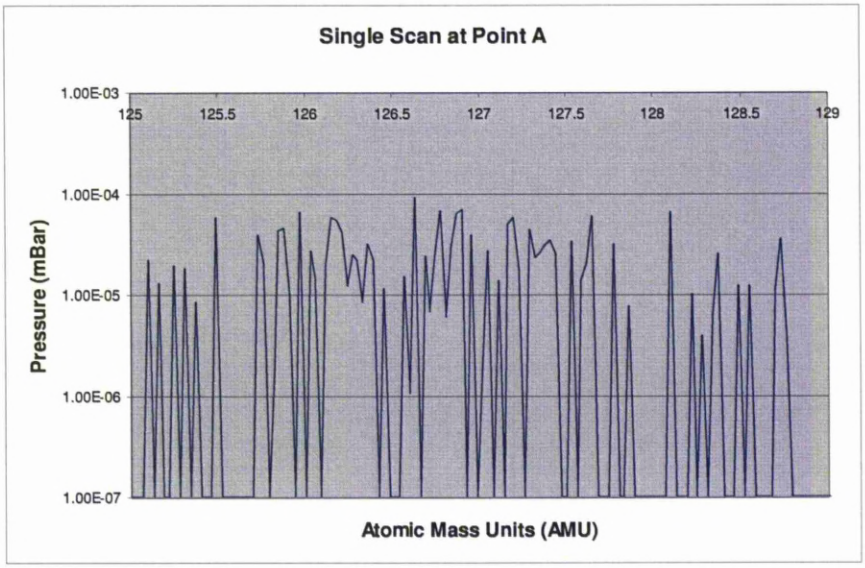


Figure 4-51: Scan 1, Point A, 20 ppm

It is difficult to make out any patterns and therefore the average of the 10 scans is calculated and the following scans are obtained.

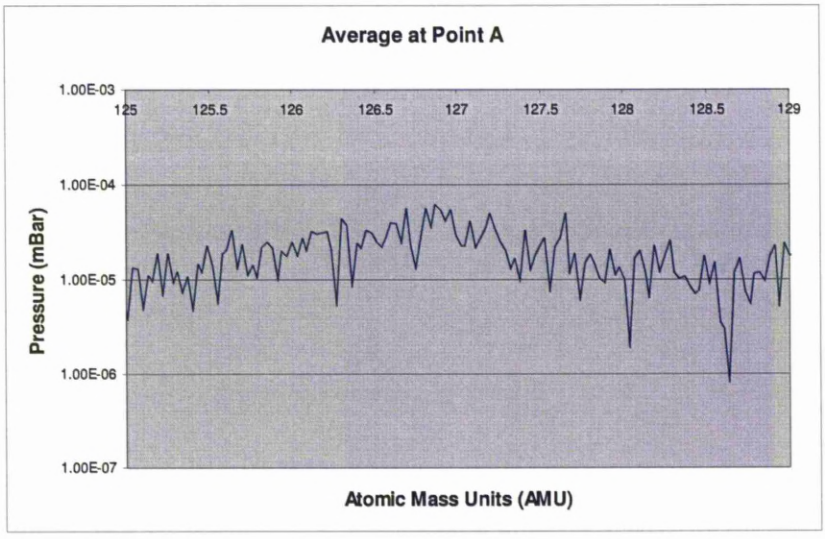


Figure 4-52: Point A Average at 20 ppm

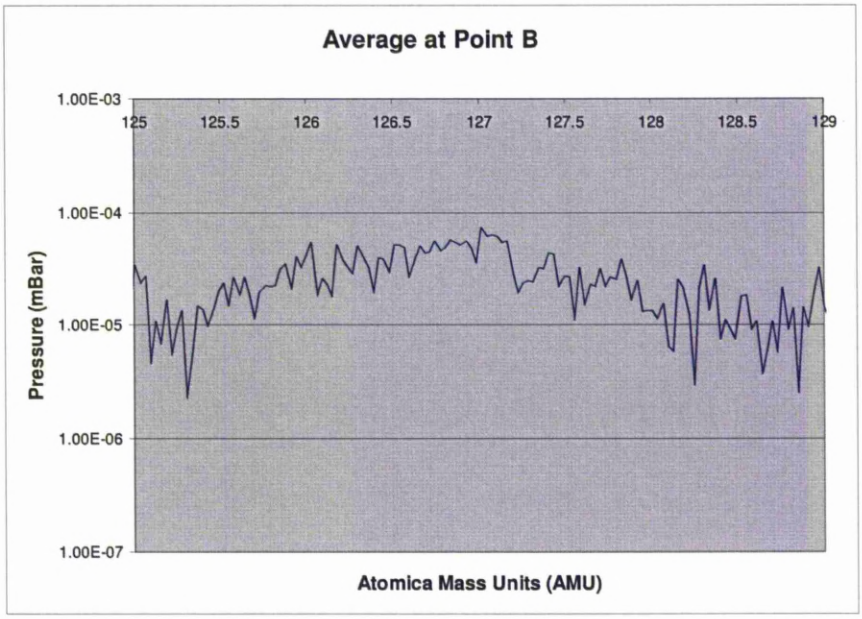


Figure 4-53: Point B Average at 20 ppm

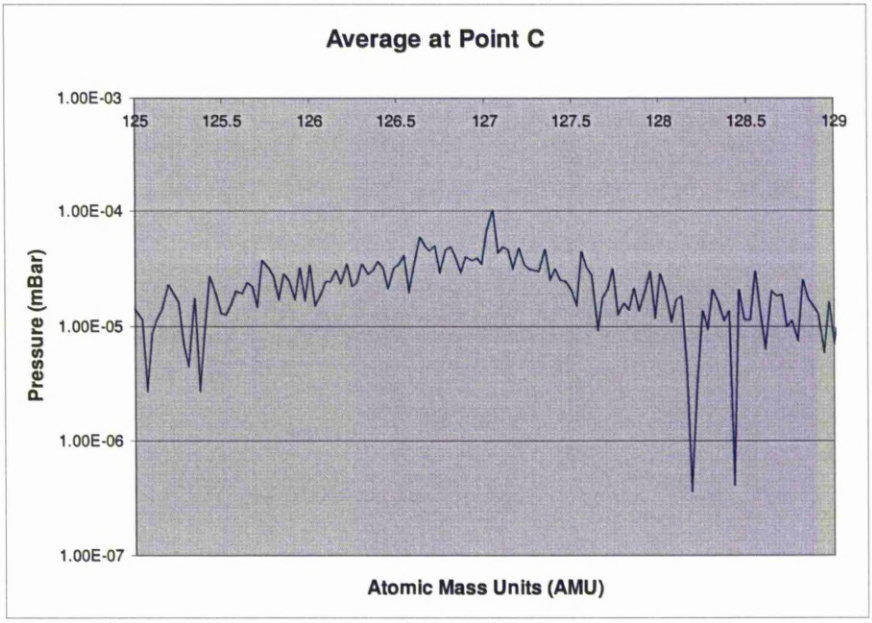


Figure 4-54: Point C Average at 20 ppm

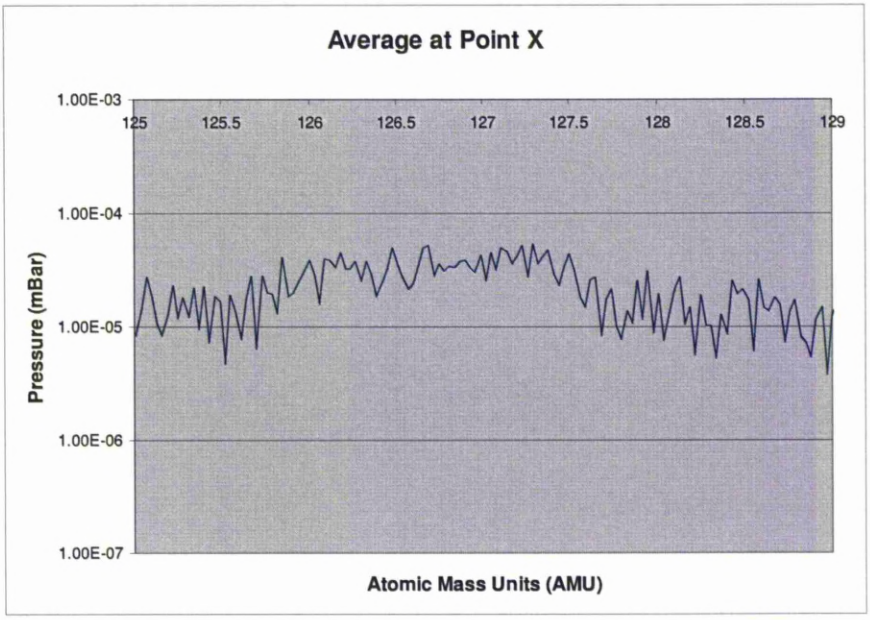


Figure 4-55: Point X Average at 20 ppm

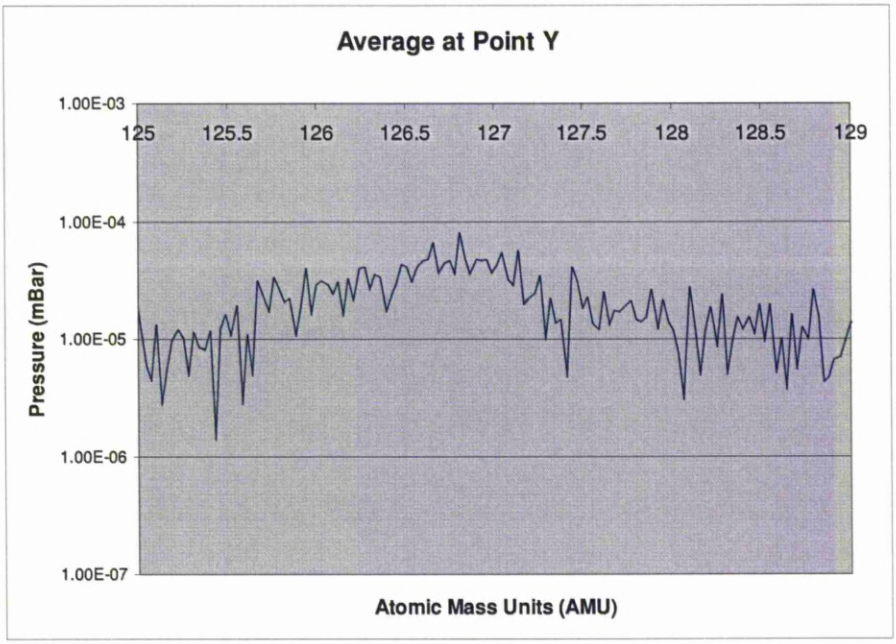


Figure 4-56: Point Y Average at 20 ppm

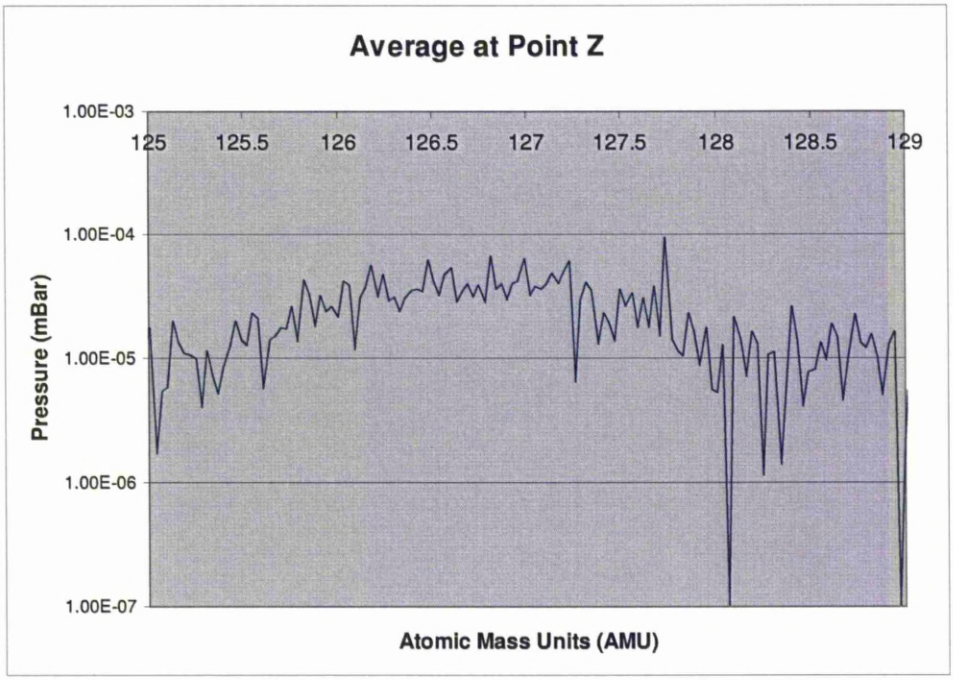


Figure 4-57: Point Z Average at 20 ppm

It can be seen that even at low concentrations of SF_6 an SF_5^+ trend can be seen by averaging a number of scans together. As long as the source concentration does not change then the more scans that are averaged together then the better the resulting scan. It is estimated that the concentration of gas at each measurement point is in the order of 500 ppb. However, at this point it is difficult to obtain the location of a leak. The scans only indicate that there is a leak present somewhere and gives the concentration of the SF_6 in air at the measurement points.

4.5 Conclusions

In this chapter it has been shown that it is possible to determine whether a gas discharge exists close to a measurement point, and that using known quantities of SF_6 in air and comparing them with the SF_5^+ peaks it is possible to obtain calibration data so that indications of concentration can be obtained. However, using this data alone it is not sufficient to establish how close or far it is from that measurement point and also how strong the leak is. In other words the data does not give the size and location of a leak, the only parameter that may be obtained is the concentration of SF_6 in air at the measurement point. Concentrations of SF_6 in air have been successfully identified on site at a working power station.

It has also been seen that the transit time will affect readings depending on how far away from a measurement point a gas discharge is. This means that if multiple measurement points are used then gas will take different amounts of time to reach each point. The raw data taken from the mass spectrometers must be manipulated in order that the position and approximate size of a gas discharge may be obtained.

Data has been taken at 6 tri stimulus measurement points and concentrations of sub parts per million were detected in air. The tests conducted used sources of 200 to 20 ppm over short distances. This implies pure SF_6 leaks

may be detected at a reasonable distance. It has been proven that techniques such as averaging scans together and eliminating negative pressure peaks that concentrations of SF_6 under 1 part per million in air can be detected

It has been shown that using a single mass spectrometer, multiple measurement points can be utilised to give more comprehensive data about a two dimensional or three dimensional spaces. However, when samples are taken from more than 3 points etc. the data obtained increases and becomes less manageable and more complicated. This makes it increasingly difficult to determine the position of Leaks and the concentration of SF_6 in air at the source point.

The data that has been obtained in this chapter gives indications only and it is difficult to analyse multiple graphs and scans in order to build up a profile of SF_6 in a space. Chapter 5 takes the scans recorded in this chapter and performs a chromatic analysis on them.

Chapter 5 – Analysis and Discussion

This Chapter is concerned with chromatic analysis and interpretation of results in the chromatic domain to yield an understanding of the systems behaviour. The tests performed in Chapter 4 are analysed using chromatic methods and processed to give HLS Values. These Tristimulus chromatic values are represented on a pair of polar plots HL & HS and discussed.

5.1 Introduction

A Monitoring system has been developed and tested to detect SF_6 leaks from high power equipment. The system makes use of the measurement capabilities of a mass spectrometer. Results have been presented in Chapter 4. These results were presented in the form of mass spectra which indicate the concentration of SF_6 in air. However, to aid the interpretation of the complex data information extraction can be performed on the data scans using the chromatic techniques described in Chapter 2. The processed mass spectrometer data is represented on a pair of polar plots. The polar plots are used to yield signatures for different concentrations of SF_6 and also assess the position, concentration and spread of leaks.

5.2 Chromatic Methods

The mass spectra scans taken when measuring gases using the two dimensional model in the previous chapter are complicated. Using these scan it is possible to determine which pipe detects the highest concentration peak and then using the transit times it may be possible to estimate which detector the leak is closest to. However, in practise the transit time to each detector is different and the gas disperses. Therefore over large distances these estimates become more difficult. The scans contain much more information which is not being utilised and simplified visualisation of the data via the chromatic method may identify trends here to hidden. The chromatic method can be applied in a number of ways. This chapter describes two approaches which may access the information.

5.2.1 Triangle Filters

The chromatic technique may be applied to single SF_6 fragmentation peaks in order that it may be possible to detect lower concentrations of gas. This is done by obtaining signatures for different concentrations of SF_6 so that signals may be extracted from the noise by identifying emergent patterns. The shape and application of the chromatic filters may be changed to alter sensitivity to changes the signal. Two different approaches are discussed, these are;

- Shifting a truncated Triangle filter across a scan
- Applying a fixed Gaussian Truncated Triangle Filter over a fixed mass range.

The chromatic filters are applied to mass spectra data to obtain RGB values which are converted to HLS. This data is presented in the form of a pair of polar plots, HL & HS.

5.2.2 Spatial Application

As described in Chapter 2 the deployment of sampling tubes spatially combined with the application of the chromatic approach may provide a better indicator of where a gas originates and also what the concentration of that gas in air is at the source. This Chapter describes how the mass spectra data taken over a fixed range about an SF_5^+ peak at each of the measurement points on the tristimulus system is used as to produce RGB and hence HLS values. The data is presented in the form of a pair of polar plots HL & HS and is discussed.

5.3 Triangle Filter Application

5.3.1 Introduction

One of the main problems when using a mass spectrometer to detect leaks is that concentration levels can be small. The smallest concentration that the mass spectrometers have been able to measure using the calibration results obtained in Chapter 4 has been of order of 0.5 ppm. The following section describes how chromatic filters can be used to identify patterns in spectra in order that it may be possible to detect smaller concentrations of SF_6.

As described in chapter 2, the three overlapping Gaussian filters used for chromatic monitoring can be optimised with the best linearity occurring when the individual filters are spaced 2σ apart *Dean* [1] and they are in the form of truncated triangle filters. The triangle filters in chapter 2 were normalised to a Y-axis between 0 and 1 and on the X-axis between 0 and 50, however, these values can be changed to accommodate the data as required. The filters can be applied to data in a number of ways and the following section describes the two applications that this project is concerned with.

5.3.2 Shifting a Truncated Triangle Filter

5.3.2.1 Introduction

A balloon filled with SF_6 is placed next to the inlet of the CIRRUS mass spectrometer and allowed to empty via a small hole. The amount of SF_6 reaching the mass spectrometer decreases over time. The mass spectrometer is set to continuously monitor the SF_5^+ peak only. A truncated RGB triangle filter with a width of 1.5 AMU and amplitude normalised to the maximum value of the SF_5^+ peak detected is applied to the series of SF_5^+ scans. The HLS values are calculated for each scan and the scan results are presented together with their associated HL and HS plots. The triangle filter is applied from 124 AMU. Values for R, G & B are obtained by integrating the signals together as described in Chapter 2. After the R, G & B values are obtained the triangle filters are moved 0.5 AMU to the right and the new RGB values are calculated. This process is repeated until the triangle filter has passed the SF_5^+ peak and beginning of the filter starts at 128 AMU, Figure 5-1.

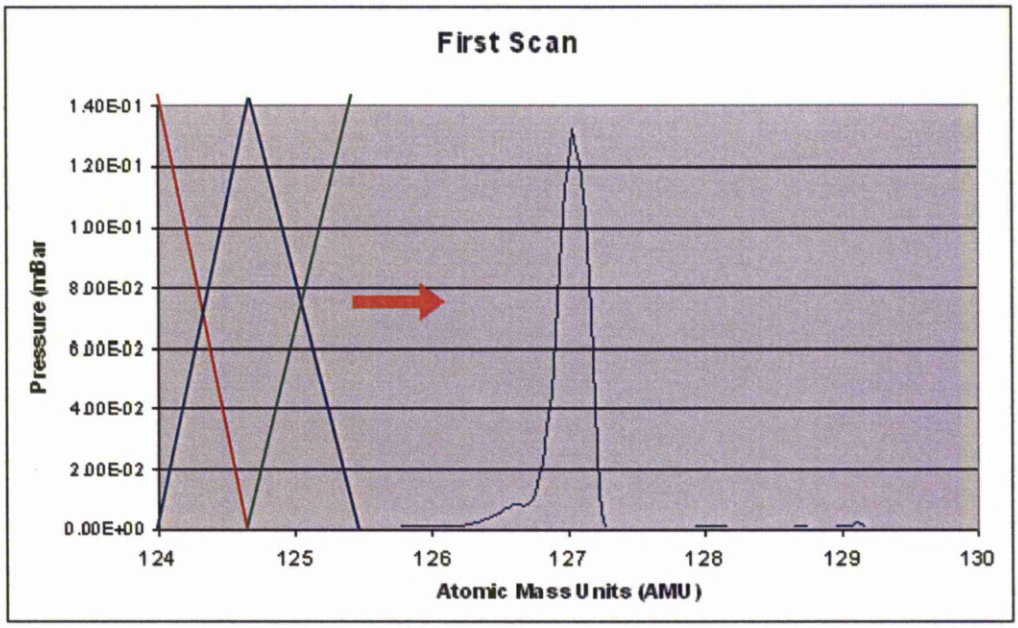


Figure 5-1: Shifting Filter applied to a Single SF_5^+ peak

The Hue, Saturation and Lightness Values are calculated by using the RGB values obtained and the equations described in Chapter 2 so that the HL and HS plots can be ascertained. Scans 1, 2, 40, 47, 52 and 60 are chosen from a total of 60 scans so as to give a good range of SF_6 concentrations and noise levels. No scans were chosen between 2 and 40 as they were all very similar. The data in Figure 5-1 is displayed using a linear axis for the pressure. However, some scans presented use a logarithmic vertical scale in order that the peaks due to the Isotopes of Sulphur can be seen.

5.3.2.2 First Scan

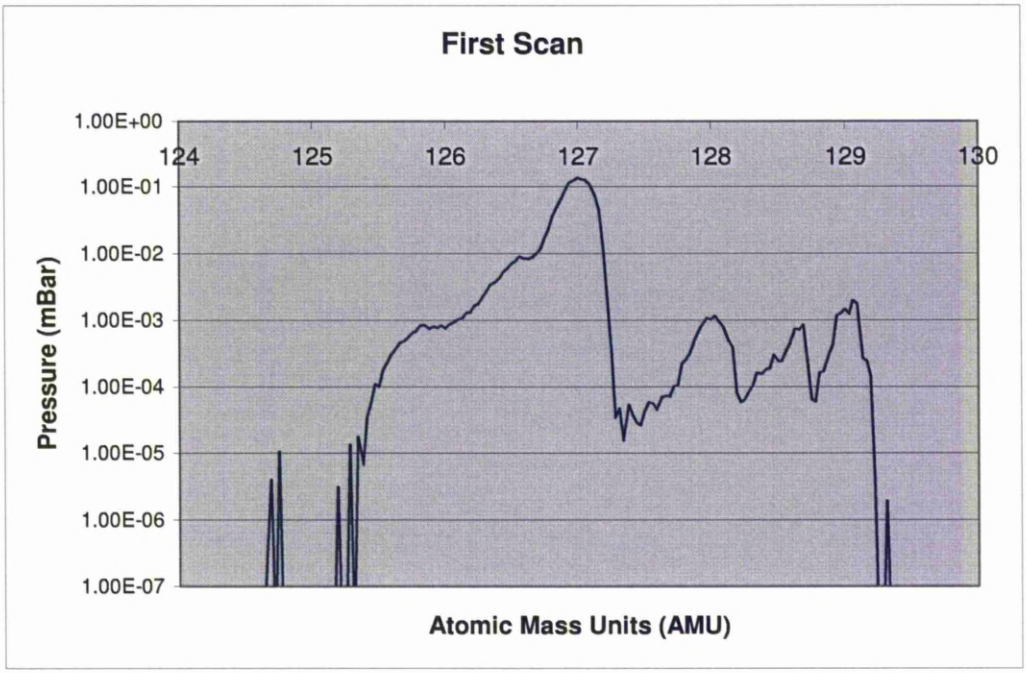


Figure 5-2: Mass spectrum for Scan 1

Figure 5-2 shows the first mass spectra scan that was obtained and it can be seen that there are a number of peaks and that the SF_5^+ peak (127 AMU) is the largest. From calibration it is estimated that the peak represents a concentration of SF_6 in air of approximately 1500 parts per million. The peaks between 128 and 129 are due to the Isotopes of Sulphur. As the concentration of SF_6 in air reduces, the peaks due to the Isotopes of Sulphur will reduce into the noise to leave only

the SF_5^+ peak visible. Figure 5-3 and Figure 5-4 show the HL & HS plots that are derived from applying the truncated filter.

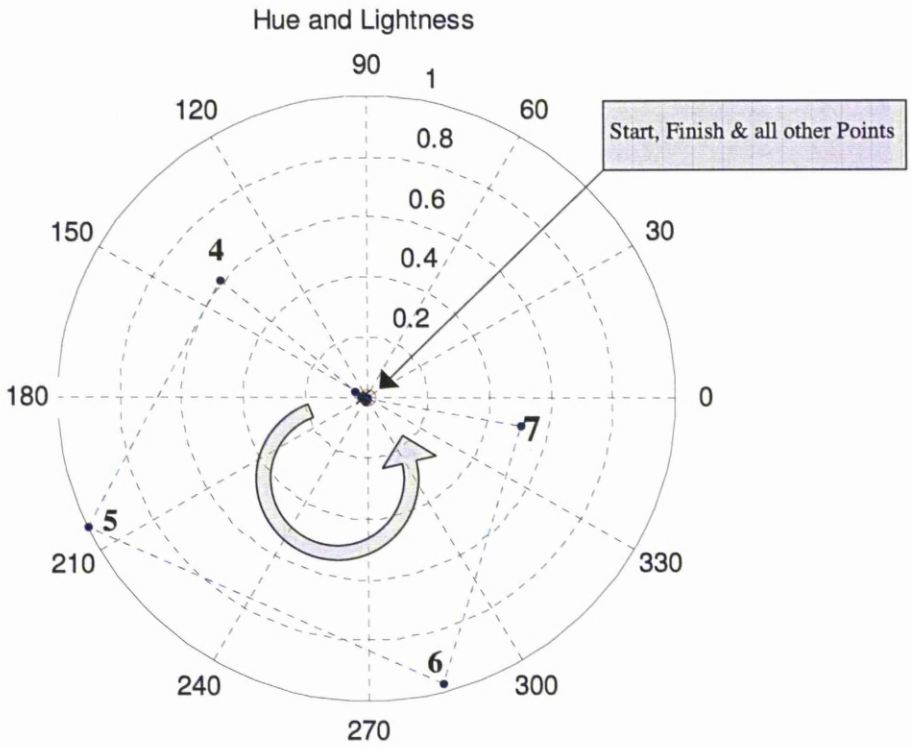


Figure 5-3: Hue- Lightness Plot

The plot in Figure 5-3 contains 11 points that have been calculated for each filter step. The majority of the points are located at the centre of the polar plot and although it is difficult to see, the start and end point are represented by a cross for the start and a circle for the end which are all at the centre. As the filters are stepped across the SF_5^+ peak the first data point to emerge from the centre is

data point 4. This is the point at which the triangle filter first overlaps the peak. The data then travels in the direction of the arrow to points 5, 6, 7 and then collapses back to the centre again. At first glance the signature that the points produce looks symmetrical however point 7 is a little closer to the centre than point 4. The reason for this is that the SF_5^+ peak has a gradual rise time and a sharp fall off so that there is a stronger signal within the triangle filter at point 4 than there is at point 7. Figure 5-4 highlights the difference in signal within the filters with the black area representing the data within the filter at point 4 and the white area the data within the filter at point 7. The figure is displayed using a linear scale for the pressure axis since the polar plots are also derived from the linear data. The Isotopes can just about be made out at mass 128 and 129 but the peaks are small in the linear scale and do not contribute a great deal to the area under the graph within the filters.

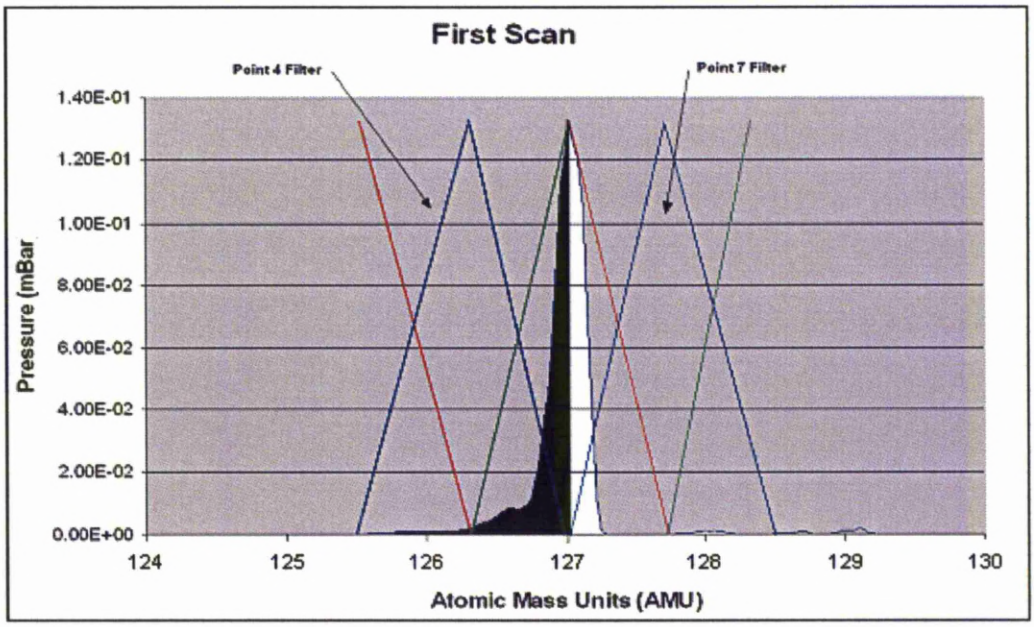


Figure 5-4: Data within Filters

If the rise time was more gradual then it would be expected that point 4 would move out towards the circumference of the plot and alternatively if the rise time was sharper then it would move towards the centre. Also, if the Isotope peak at 128 AMU was larger then it would be expected that point 7 would move towards the circumference of the plot.

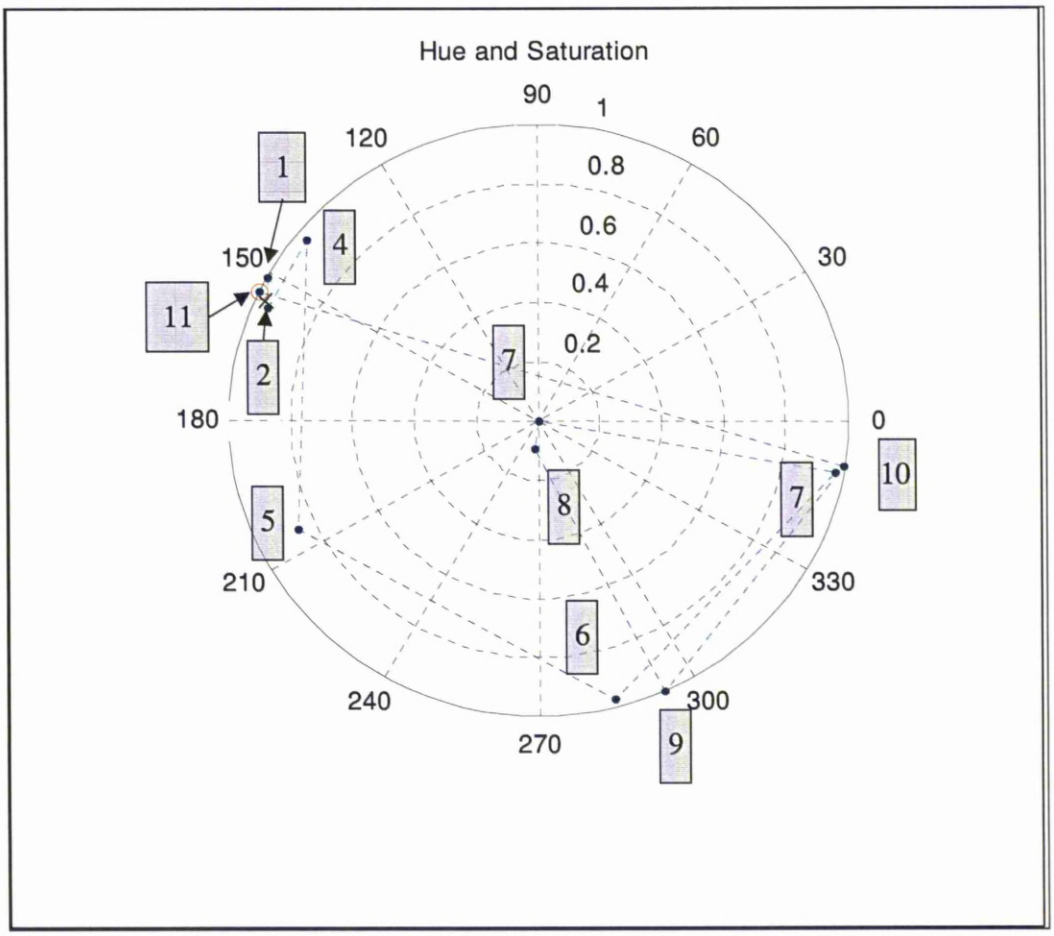


Figure 5-5: Hue-Saturation plot

The start point 1 on the HS plot, Figure 5-5, is represented by a cross and the end point 11 is represented by a circle. It can be seen in Figure 5-5 that points 1, 2, 3 and 11 are all in the same vicinity. The reason for this is that at these points the filters are place over areas of the scan in which the signal is low. The Hue is the dominant wavelength which will change as the filters shifts along the scan and the saturation is an indication of the spread in the masses. A saturation value of 1

will indicate a single mass and zero indicates that all mass are present with the selected range.

5.3.2.3 Second Scan

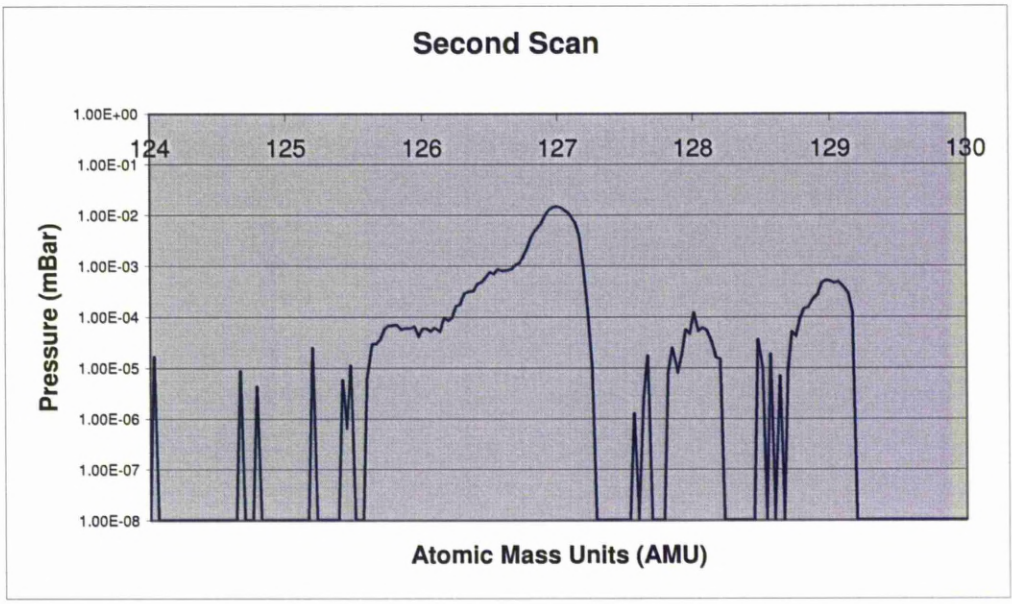


Figure 5-6: Mass Spectrum for Scan 2

Figure 5-6 shows the second mass spectra scan obtained. From calibration the SF_5^+ peak is in the order of 110 PPM. It can be seen that the Isotope peaks have already reduced considerably, however, the gradual rise and sharp fall off around the SF_5^+ peak is still present and it is expected that the H-L plot will again be slightly asymmetrical. Figure 5-7 shows the resulting H-L & H-S plots that are obtained after applying the truncated triangle filter.

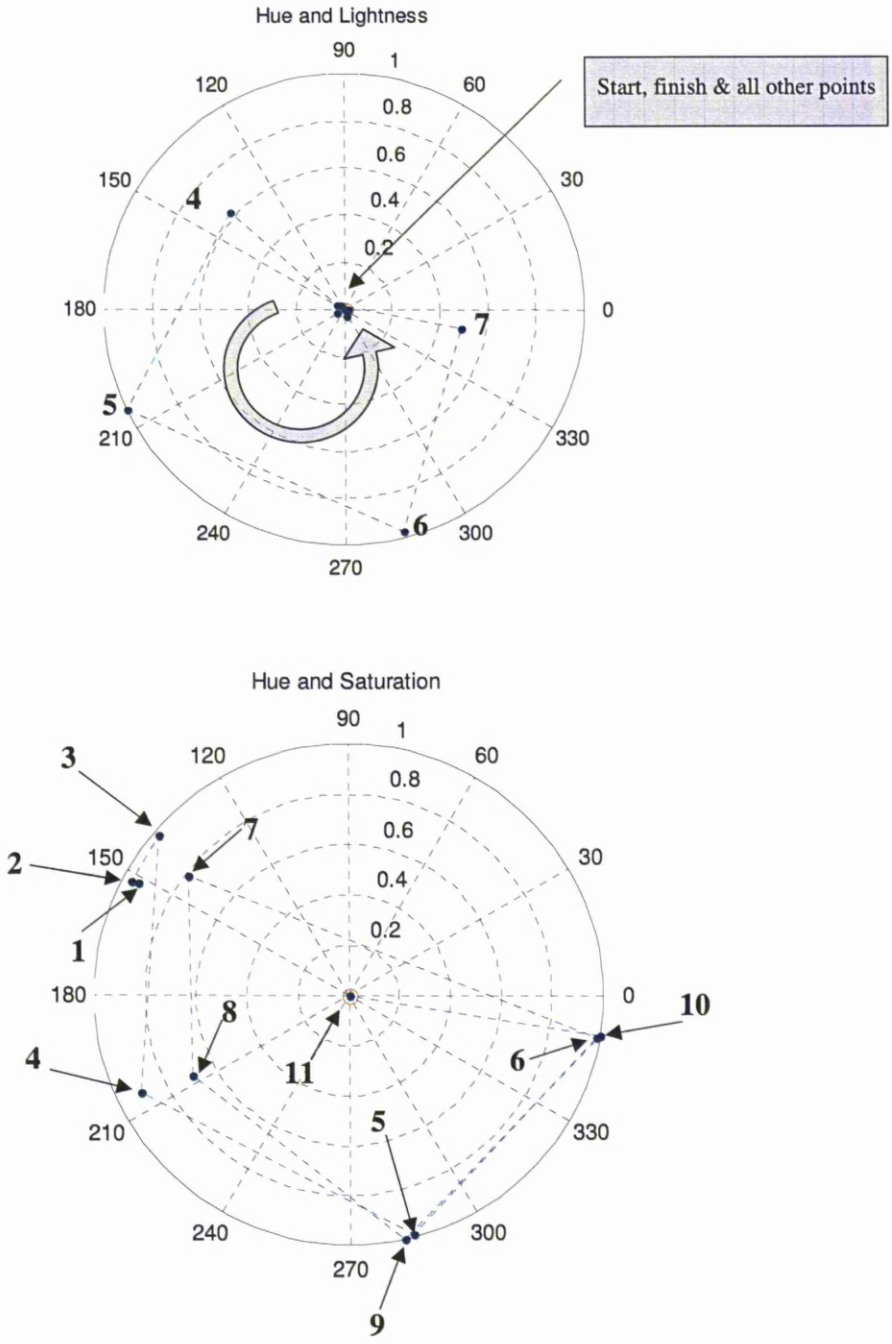


Figure 5-7: H – L and H – S plots for Scan 2

The H-L plot for the second scan looks almost identical to the plot for the first scan; however, the H-S plot has changed. The points are very similar for 1, 2, 3, 4, 5 and 6 but 7 and 8 have moved out from the centre. Also, points 9 and 10 are at a similar place but point 11 has now moved to the centre of the plot.

5.3.2.4 Scan 40

After 40 scans the measured SF_5^+ partial pressure has reduced to below $1x10^{-3}$ mbar, Figure 5-8. The HLS values are derived and Figure 5-8 and Figure 5-9 show the scan and resulting H-L and H-S polar plots.

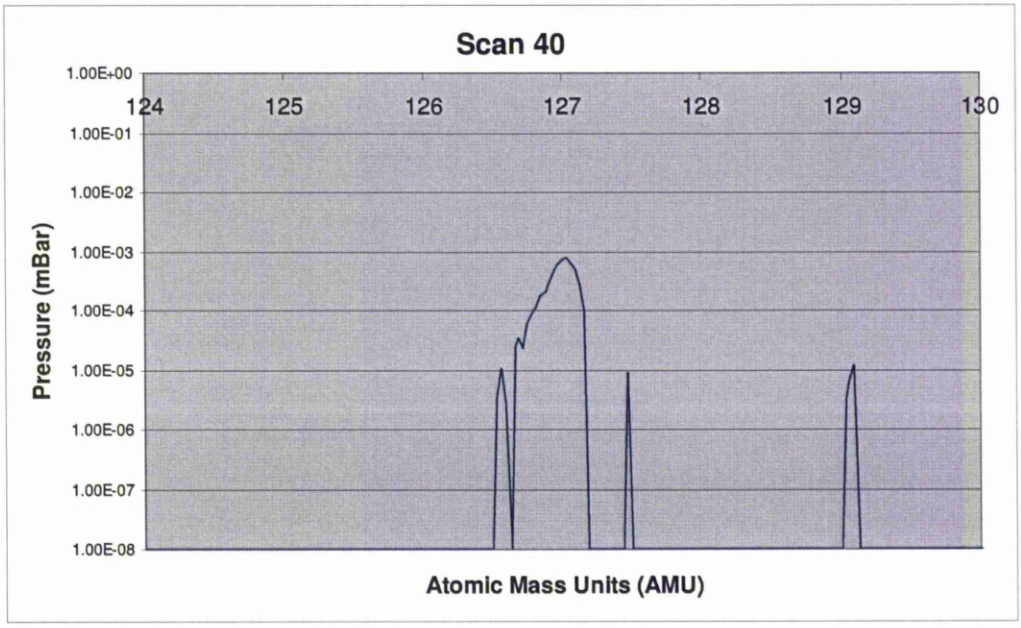


Figure 5-8: Mass Spectrum of Scan 40

The Isotope peaks are extremely small now and it is not certain that the peak at 129 AMU is noise or a small isotope peak. The reason that no other peaks can be seen it that any negative peaks which the mass spectrometer recorded where assumed to be 1 x 10^{-8} mBar and the mass spectrometer did not give any values lower than 1 x 10^{-7} on this particular scan. 1 x 10^{-7} is equivalent by calibration to approximately 1 part per billion or 0.001 PPM..

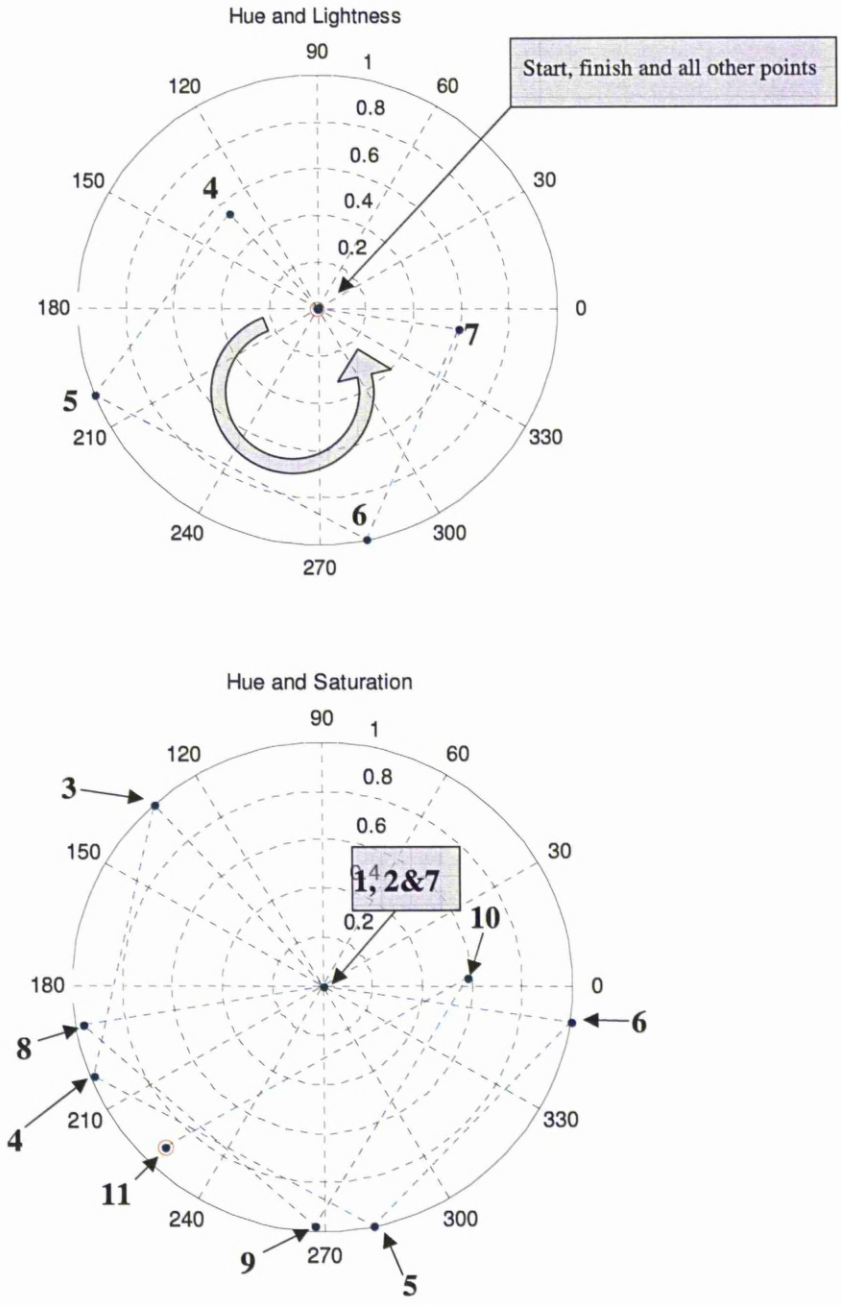


Figure 5-9: H – L and H – S plots for scan 40

The H-L plot for scan 40, Figure 5-9, again is very similar to the plots obtained for scan 1 and scan 2 and it can be seen that this shape on a plot is a characteristic of SF_6. Also, it should be noted that since the rise is becoming sharper similar to that of the fall rate that the plot is looking a lot more symmetrical than the previous plots. The shape that the H-S plot produces again is different to the previous plots however points 3, 4, 5 & 6 are in a similar position as before which means that the sections of the graph that the filters cover have similar characteristics regardless of the concentrations of SF_6. The reason that points 1, 2, 7, 8, 9 & 10 vary in position is due to the noise produced by the mass spectrometer.

5.3.2.5 Scan 47

Figure 5-10 shows the Mass spectra data that was recorded in Scan 47. The SF_5^+ partial pressure peak is approximately 2.5 x 10^{-4} mBar which from calibration implies a concentration of SF_6 in air of 2 PPM. Unlike scan 40 the noise level for this particular can is relatively higher as various partial pressure spikes can be seen elsewhere on the scan.

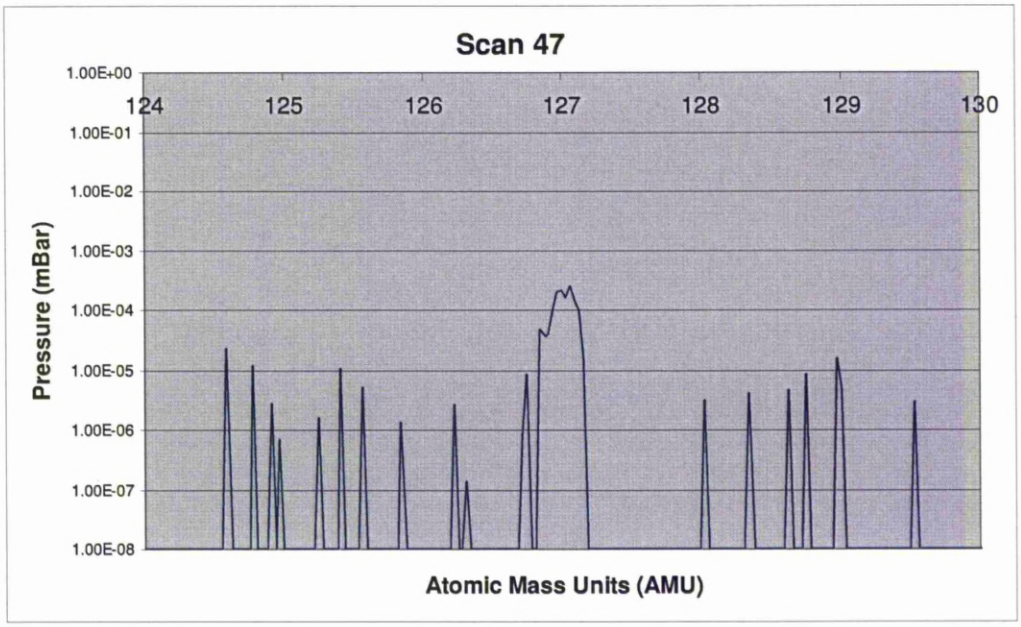


Figure 5-10: Mass Spectrum for Scan 47

The noise level for this scan is up to 1 x 10^{-5} mBar as seen by the peaks around 127 AMU. The HLS Values are calculated and Figure 5-11 shows the resulting H-L and H-S polar plots. The rise and fall gradient of the SF_5^+ partial pressure peak at this concentration are both very steep however there is a lot more noise which is now relatively close to the maximum peak and this may affect the symmetry of the H-L

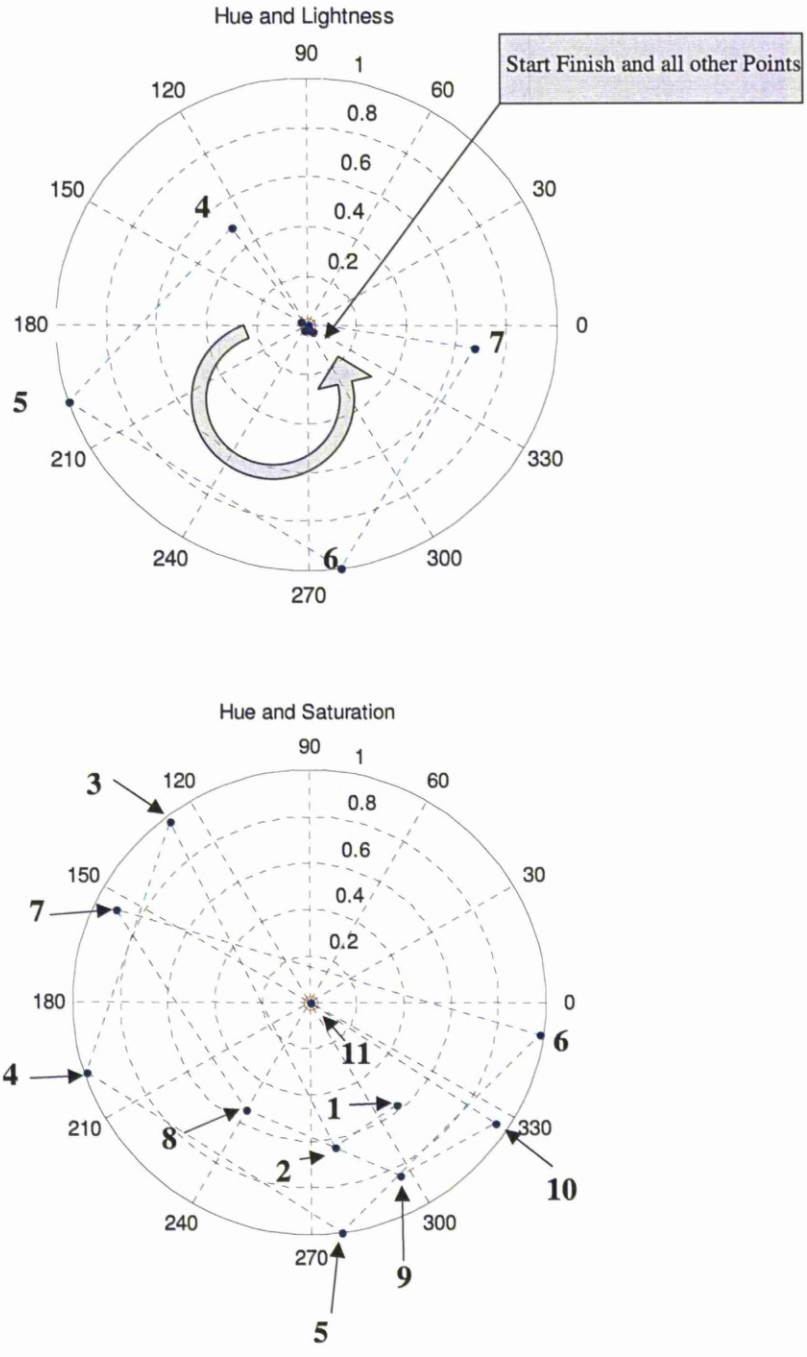


Figure 5-11: H – L and H – S plots for Scan 47

The SF_6 signature shape is still a consistent in the H-L plot and it is very easy to tell that SF_6 is present. The saturation levels at points 4 and 7 a similar due to the sharp rise and fall however the hue has now changed due to the noise level increasing and so the shape has become more asymmetrical. H-S plots is more complicated mainly due to the increased noise level during this particular scan however again the points 3, 4, 5 & 6 are all positioned at the same point.

5.3.2.6 Scan 52

Figure 5-12 shows the 51st mass spectra scan that was obtained.

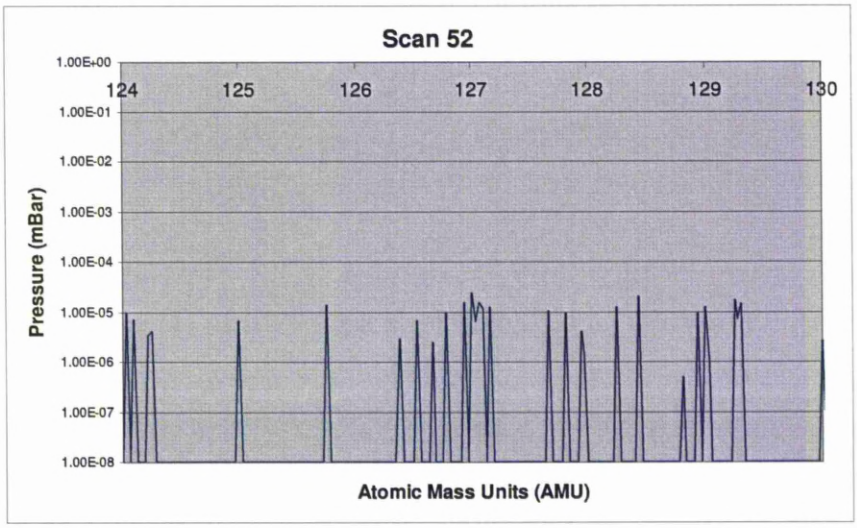


Figure 5-12: Mass Spectrum for Scan 52

If there is SF_6 present then by taking the partial pressure value at the SF_5^+ peak then it is in the order of 80 PPB (0.08 PPM). It is not obvious from the scan

that there is a definite peak at this point but this could very easily be mistaken for noise. The HLS values are calculated and the corresponding H-L and H-S plots can be seen in Figure 5-13.

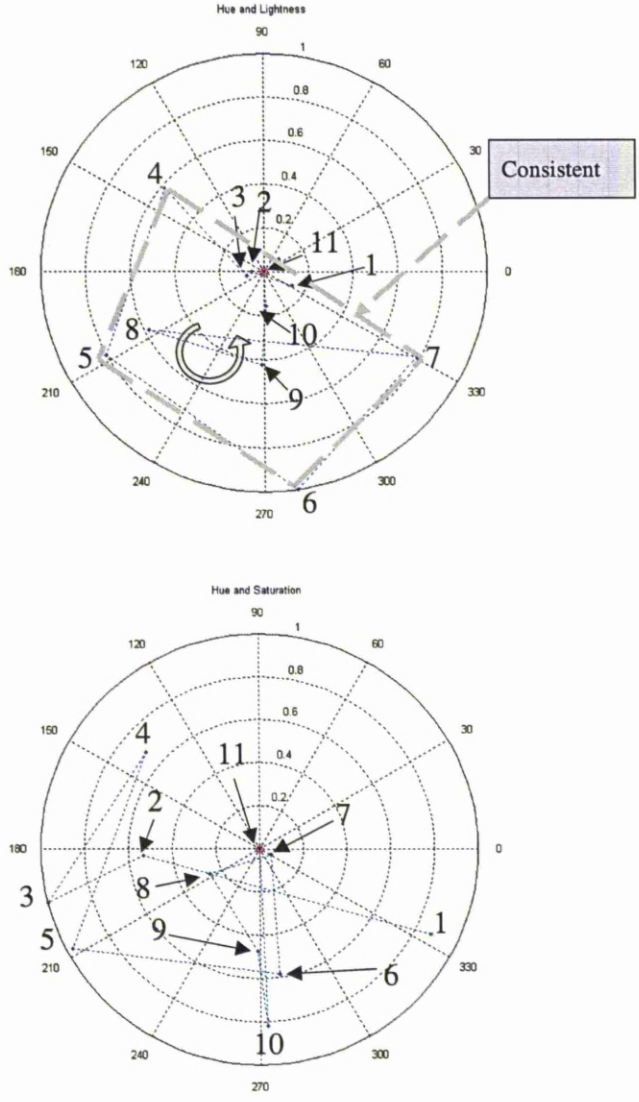


Figure 5-13: Scan 52 H-L & H-S Plots

It can be seen on the H-L plot that there is still a consistent shape which has been highlighted between the points 4, 5, 6 & 7. However points 8, 9 & 10 have now moved out from the centre. The reason for this is that now the noise levels are at a similar level to the signal itself but the SF_6 signature can still be identified. The H-S plot has now changed considerably and the shape that the points 3, 4, 5 & 6 made has now disappeared.

5.3.2.7 Scan 61

Figure 5-14 shows that mass spectrum that was obtained during scan 61 at which point the balloon had completely deflated. Although there are some peaks at 127 AMU there is no obvious SF_5^+ peak and it could easily be mistaken for noise.

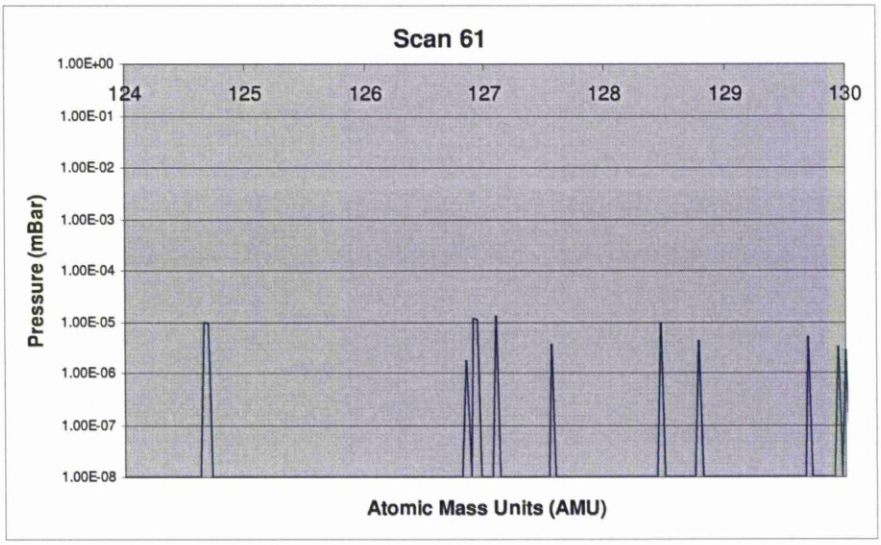


Figure 5-14: Mass Spectrum for Scan 61

From the interpretation of the scan it is almost impossible to ascertain whether SF_6 is detected. From calibration, the pressure that can be seen at 127 AMU indicates a concentration of SF_6 in air of less than 80 parts per billion. The HLS values are derived and the following H-L and H-S plots are obtained.

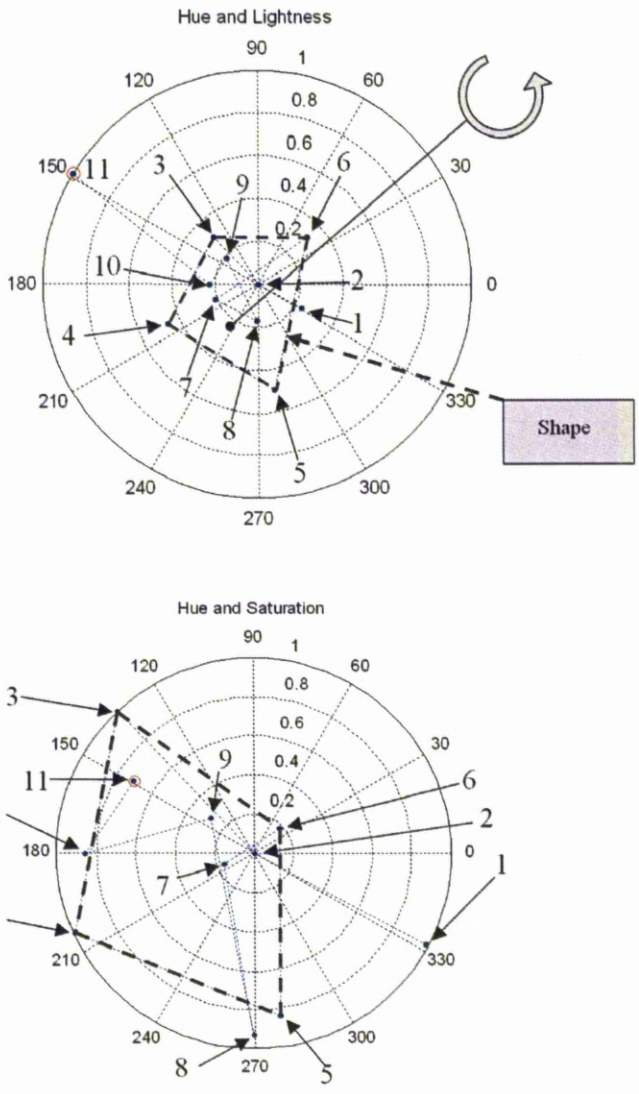


Figure 5-15: H – L and H – S plots for scan 61

The H-L plot now looks different to the previous results. The reason for this is that there is no difference between the noise and the SF_5^+ peak. However, examining the plot, at the centre there is a shape similar to the shapes present in the previous scans although with reduced light values. This may provide an indication of the presence of SF_6, The shape has started to collapse into the centre but it may be possible that by monitoring this shape can give a simple indication as to whether there is SF_6 in air at much lower concentrations than before. The HS plot is now very random due to the noise meeting the peak. However, the shape between the points 3-6 has returned.

5.3.3 Fixed Triangle Filter

5.3.3.1 Introduction

A set of truncated triangular filters, Figure 5-16, of width 1.5 AMU similar to the one used in the previous sections is applied to the mass range incorporating the SF_5^+ peak. For the tests in this section the set of filters are fixed and HLS values are obtained by integrating the filters with data taken from the mass spectrometer to obtain RGB values which are then converted to HLS data and represented in the form of H-L and H-S polar plots.

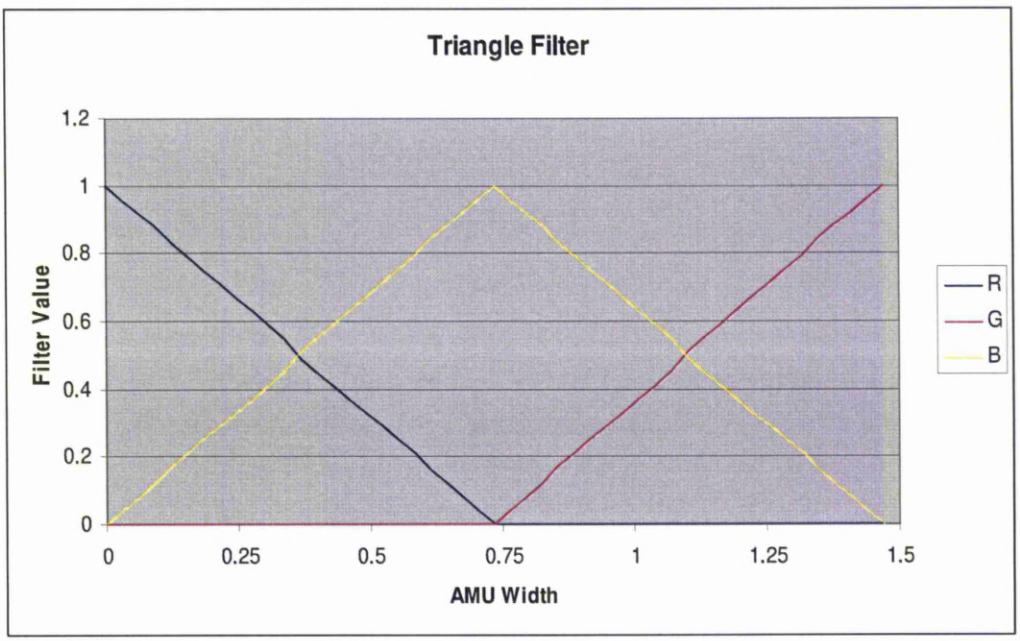


Figure 5-16: Truncated Triangle Filter

5.3.3.2 Tests

For this set of tests a gas cylinder containing 50 ppm SF_6 in air is positioned approximately 10 cm away from the opening of a tube of length 1 metre and a diameter of 0.5 mm and the valve is opened allowing the gas to migrate into the mass spectrometer. 10 scans were recorded with each scan taking approximately 30 seconds and the mass range is set from 125.5 to 128.5 AMU which is the location of the SF_5^+ peak, Figure 5-17. The triangle filter is applied to the data and Figure 5-18 and Figure 5-20 show the resulting H-L and H-S output respectively.

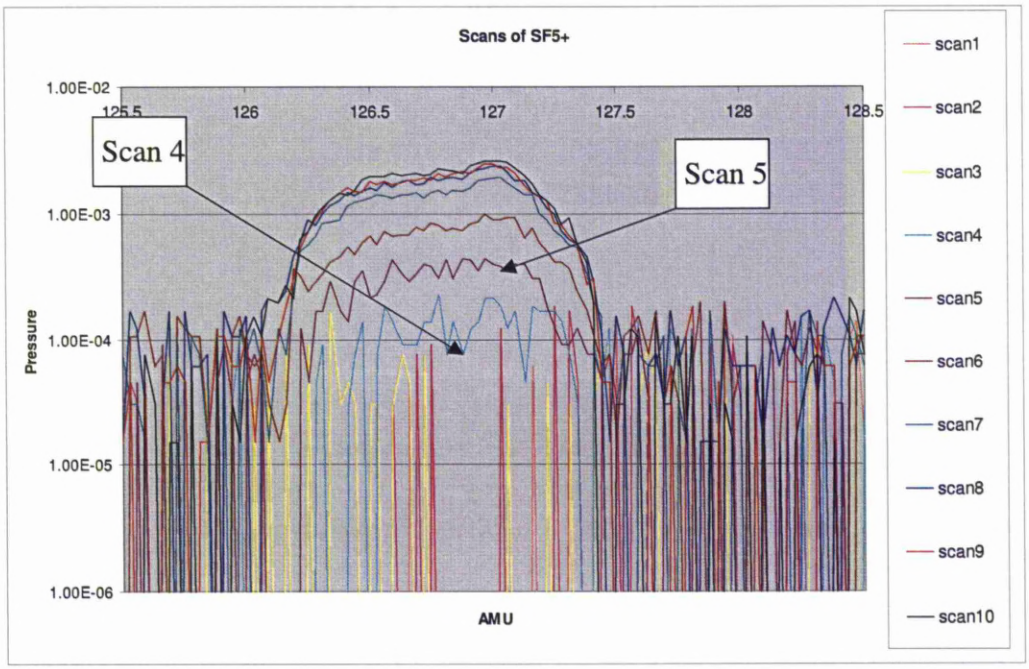


Figure 5-17: Multiple SF_5^+ peaks

The resulting scans show the how the SF_5^+ partial pressure peak reduces over time from scan 1 to scan 10. From calibration, the maximum SF_5^+ partial pressure peak indicates that there was a concentration of approximately 30 PPM SF_6 in air and that the noise level is in the region of 2 PPM. There are no Isotope peaks visible in the graph which indicates that they are buried within the noise. It can be seen that the 1st scan is within the noise and that at scan 5 the SF_5^+ partial pressure peak appears out of the noise level at approximately 5 x 10^{-4} mBar which indicates a concentration of 5 PPM and then starts to increase.

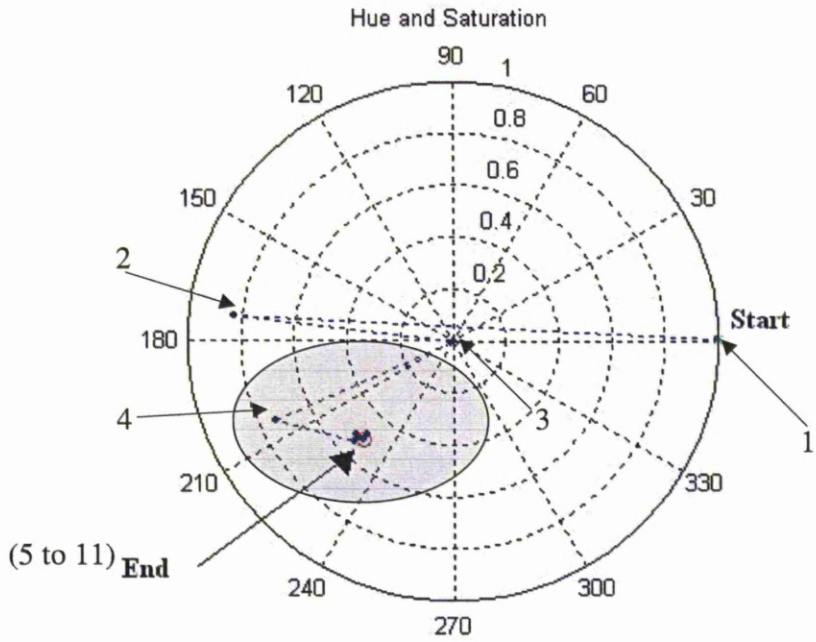


Figure 5-18: Hue – Saturation plot

The data points start at Hue = 0° and Saturation = 1 at which point no obvious SF_5^+ partial pressure peak is obvious. At this point no information can be extracted, Figure 5-19.

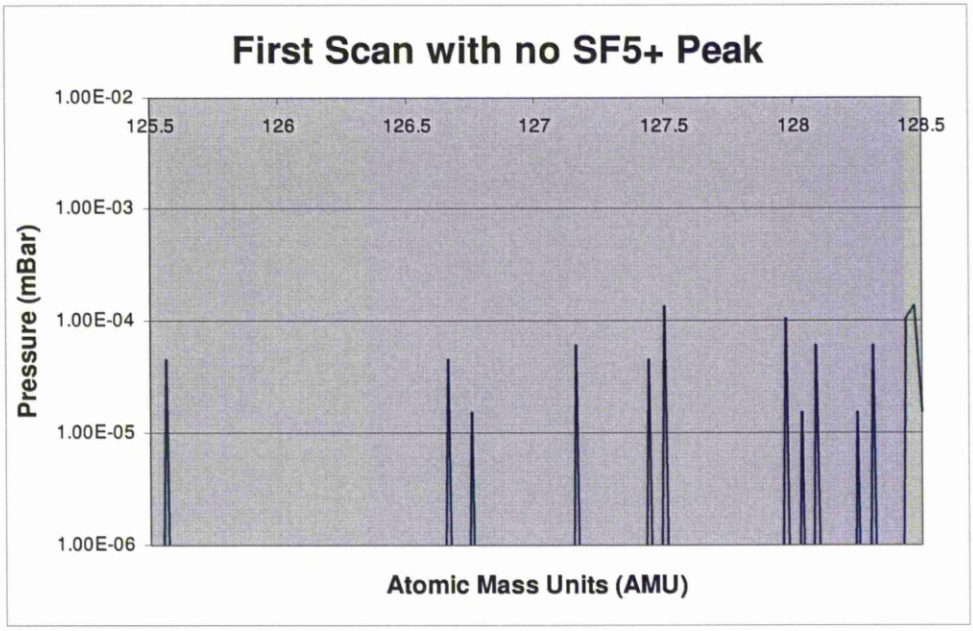


Figure 5-19: 1st Scan

The H-S values then track along to the end point where there are a cluster of data points which represent the mass spectra that have obvious SF_5^+ partial pressure peaks. However examining point 4 where the peak is not well defined it can be seen that it is within the shaded area and is in close proximity to the cluster of values with defined partial pressure peaks. If the H-S data falls within this shaded area then it this could be seen as an indication of SF_6 presence. Therefore

like the shifting triangle filters it is possible that this technique could also be used to determine the presence of SF_6.

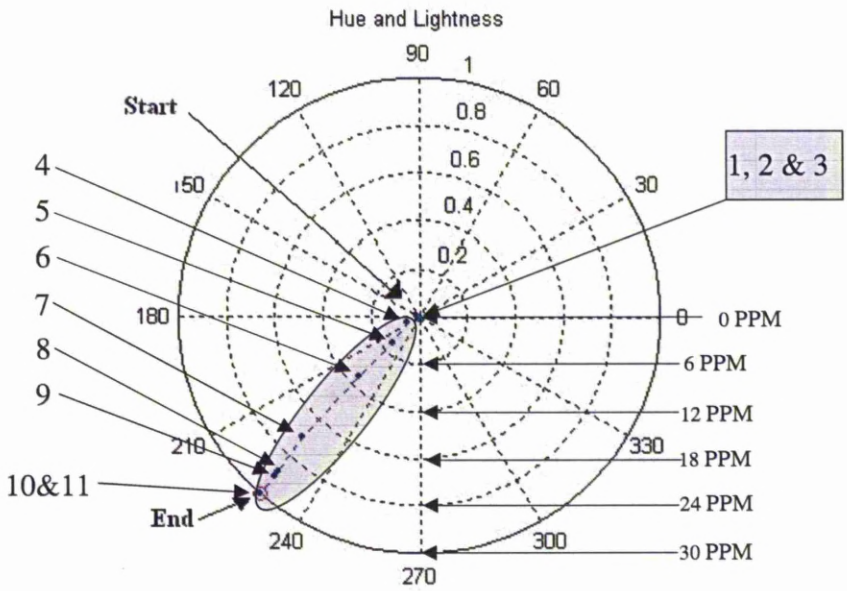


Figure 5-20: Hue – Lightness Plot

The H-L values, Figure 5-20, start at the centre and stay there until point 4 which is within the shaded area. The H-L values then start to track away and move out towards the perimeter of the plot at approximately 228°. It looks as though the Hue value does not change but it does at points 1, 2 & 3 (0°, 173°, 281° respectively) however the Lightness value is zero for these points and therefore the data appears to move in a straight line. The data has been normalised so that a saturation of 1 = 30 PPM. The concentration levels have been highlighted on the plot and have been derived from calibration.

5.4 The Two Dimensional Model

5.4.1 Introduction

The following sections describe tests and analysis on the tests that were performed in Chapter 4 on the two dimensional model using CO_2 and SF_6. For these tests, depending on which gas is to be analysed, partial pressure values are recorded at specific atomic mass units and these mass values are then used as RGB values in order to calculate the HLS values. Three tests are discussed in this section:

- A Simulate Carbon Dioxide leaks
- A simulated SF_6 Leak
- A real leak on a gas Vessel

5.4.2 Carbon dioxide Tests

In Chapter 4 a two-dimensional tri stimulus measurement system was constructed and scans were taken at three points when CO_2 was released into the air. The data obtained in these tests was used as R, G, and B values in order that

HLS data could be obtained which can be presented in the form of H-L and H-S polar plots, Figure 5-21 and Figure 5-22 respectively.

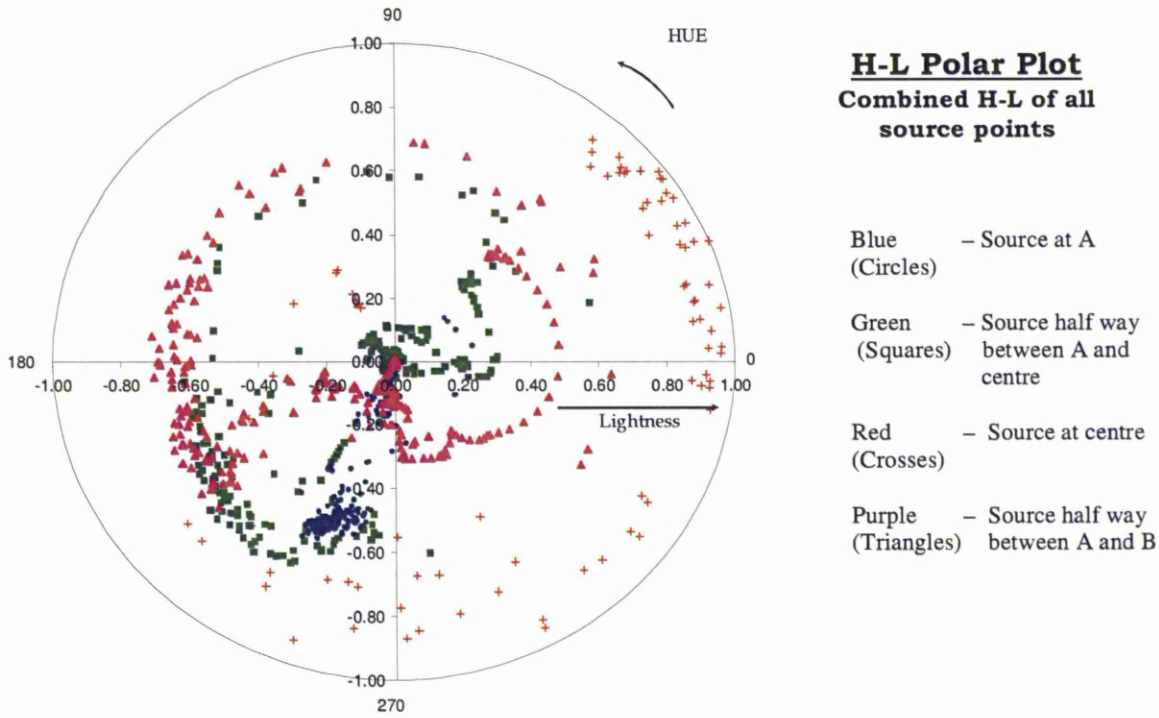


Figure 5-21: H-L plot of all source points and all data

There is a lot of information in the graph. The H-L values for the source situated at measurement point A can be seen mostly clustered together in the bottom left quadrant with some values. The data for the source half way between A and the centre and the data for the source half way between A and B can be found in all four quadrants with any Hue angle and varying lightness levels all

below 0.7. The Data for the source at the centre is spread over a large hue angle from between approximately 45° and clockwise to approximately 225° but the lightness level stays consistently above 0.7.

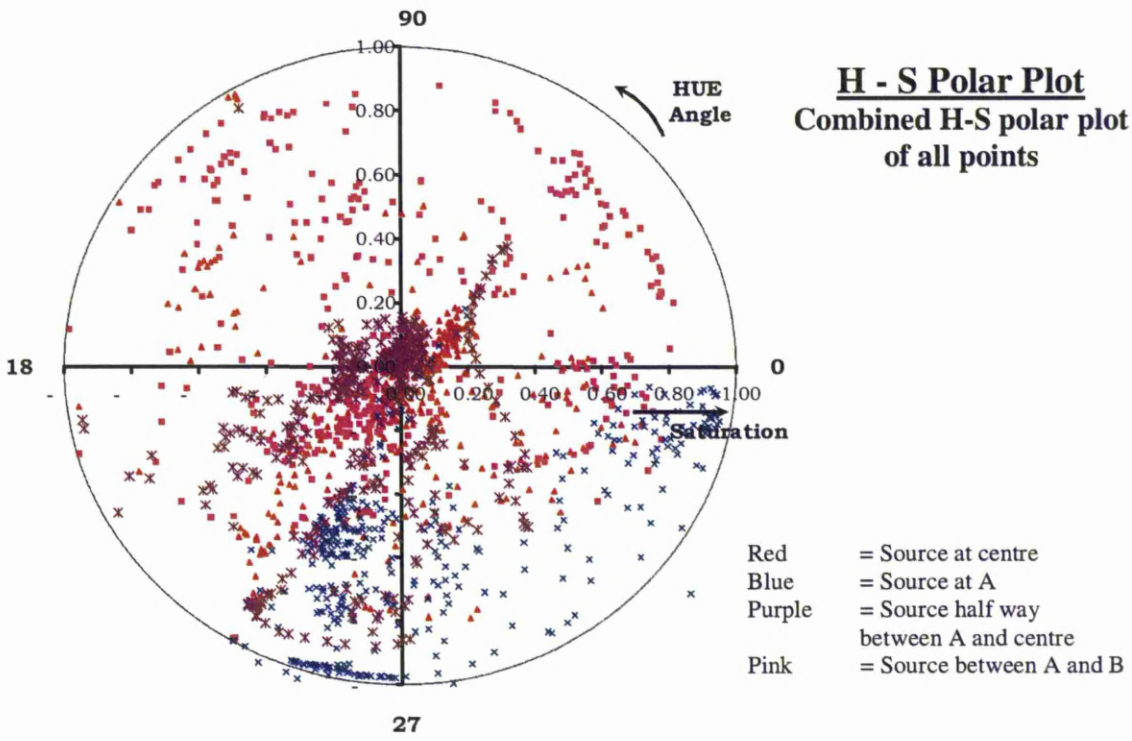


Figure 5-22: H-S plot of all source points and all data

Figure 5-22 shows the H-S data for the four tests. All of the data overlaps and appears random. The combination of Hue and Saturation should give an indication of the position of CO_2. However it is very difficult to determine position using this polar plot. The H-L and H-S plots contain complex information

about changes over a long period where there are a number of events taking place and it is difficult to extract any useful information from these figures. The events that are taking place which cause the scatter in the results have been highlighted on an example scan in Figure 5-23 and are the peak rise and peak drop off times and also the transit time for each measurement point.

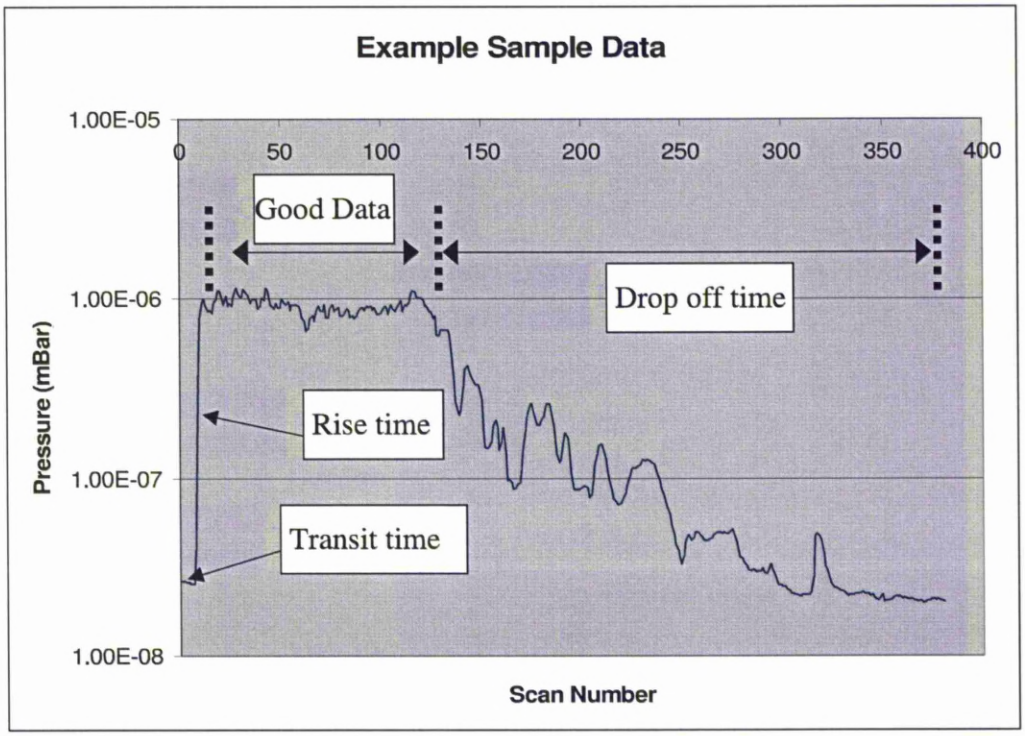


Figure 5-23: Example Sample Data

The "good data" is the data after the gas has migrated to the mass spectrometer and reached a peak level and before the partial pressure starts to fall

off. If a leak was present then it is assumed that it would only be "good data" that would be measured and that the other events in the graph are results of the test and can therefore be ignored. The following set of plots represents the results that are obtained when using only the peak values of the scans, Figure 5-24 and Figure 5-25.

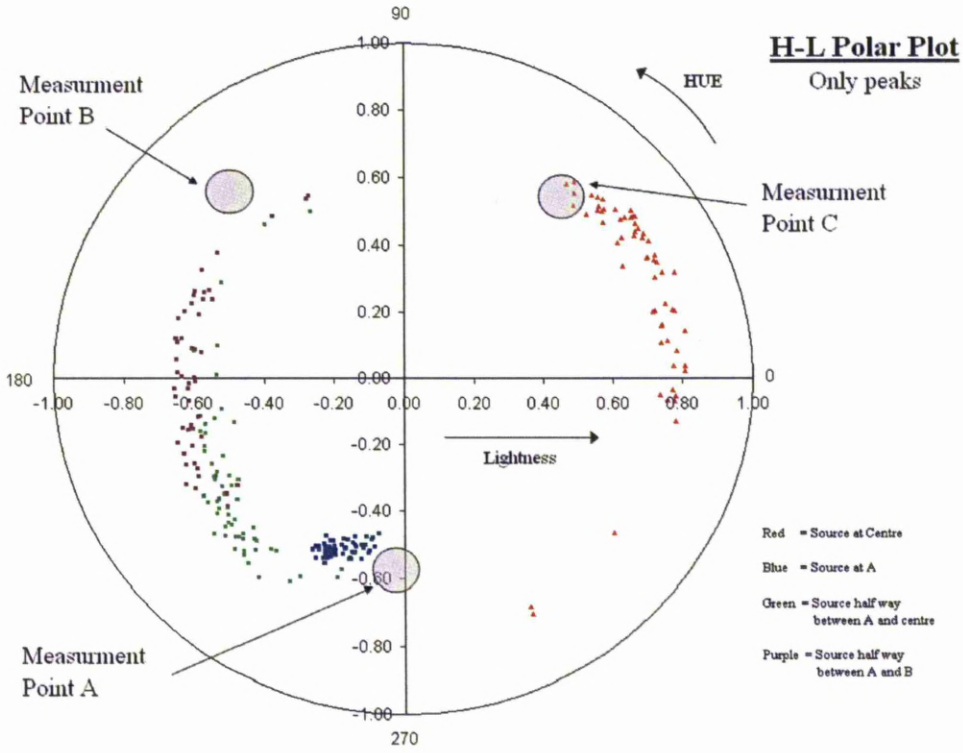


Figure 5-24: H-L Polar Plot of just peaks

It can be seen that the information on the H-L plot is now much easier to understand. The data in red represents the H-L values obtained when the leak is situated at the centre of the space and the concentration (Saturation) is consistent but the dispersion is quite varied (Hue). In an ideal situation it would be expected

the Hue values would be evenly scattered around the plot. However small drafts and the position of the nozzle will affect the dispersion and from the graph it can be seen that the nozzle must have been pointing between measurement point A and B. The purple data represents the H-L values obtained when a leak is situated half way between measurement point A and the Centre of the space and the green data represents the H-L values when a leak is situated half way between A & B. The Saturation levels indicate that the concentrations for both tests are very similar and that they are similar to the red data also. The green data indicates a larger dispersion as would be expected as the leak for this test was situated closer to measurement point B than the leak placement in the test that resulted in the purple data. Finally the blue data represents the H-L values obtained when a leak was placed next to measurement point A. It can be seen that the Saturation level again indicates the same concentration as all of the other tests and that the Hue values indicate a small dispersion. This is what is expected as the leak is place right next to the measurement point.

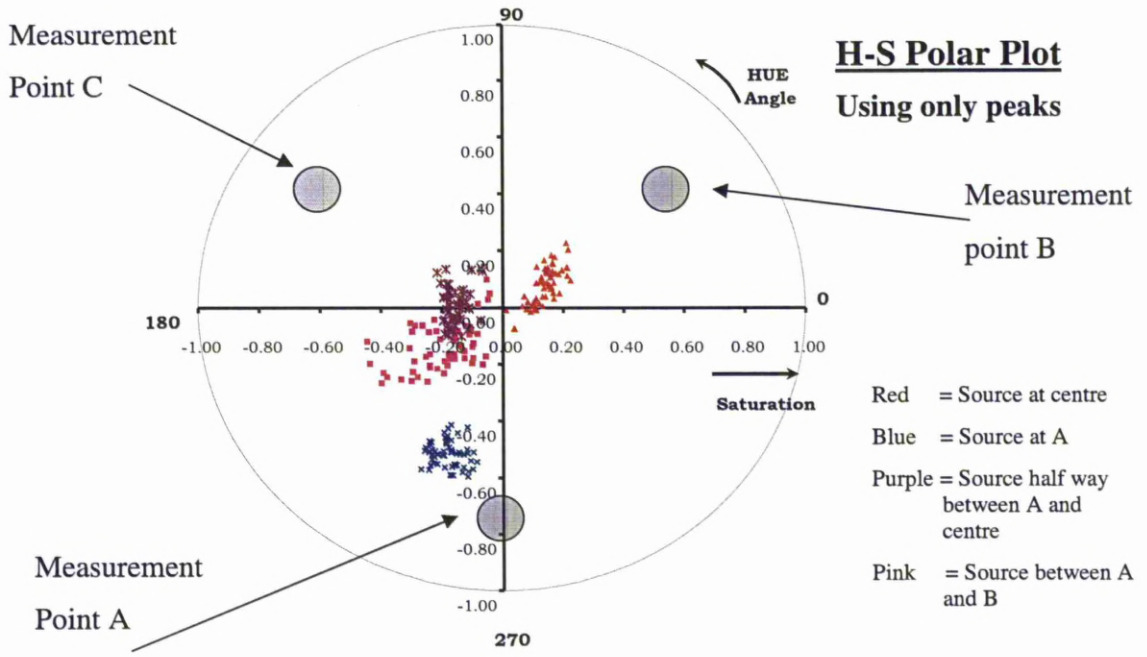


Figure 5-25: H-S Polar Plots only peaks

Similarly, the H-S values in Figure 5-25 are easier to understand than the H-S plot in Figure 5-22. Each set of data can be seen clearly and that each highlighted leak is in a similar position on the graph to what it is in the physical space.

This model was set up in a small area that contained small air currents. Therefore, drift will affect the analysis of results which is why each cluster in the plot is close to leak source but all seem to be a little to the left of the plot indicating a slight air current blowing from right to left. However, the indications are good that this method may be used to identify a leak source and concentration.

5.4.3 HLS Interpretation of small gas vessel tests

Following the successful results that were obtained by applying the chromatic technique to the CO_2 model tests, the same technique is applied to scans that were taken when monitoring for SF_5^+ around a small gas vessel with a known leak which is near to point C as described in Chapter 2. The SF_5^+ partial pressure peak data is converted HLS. The H-L and H-S plots can be seen in Figure 5-26 and Figure 5-27.

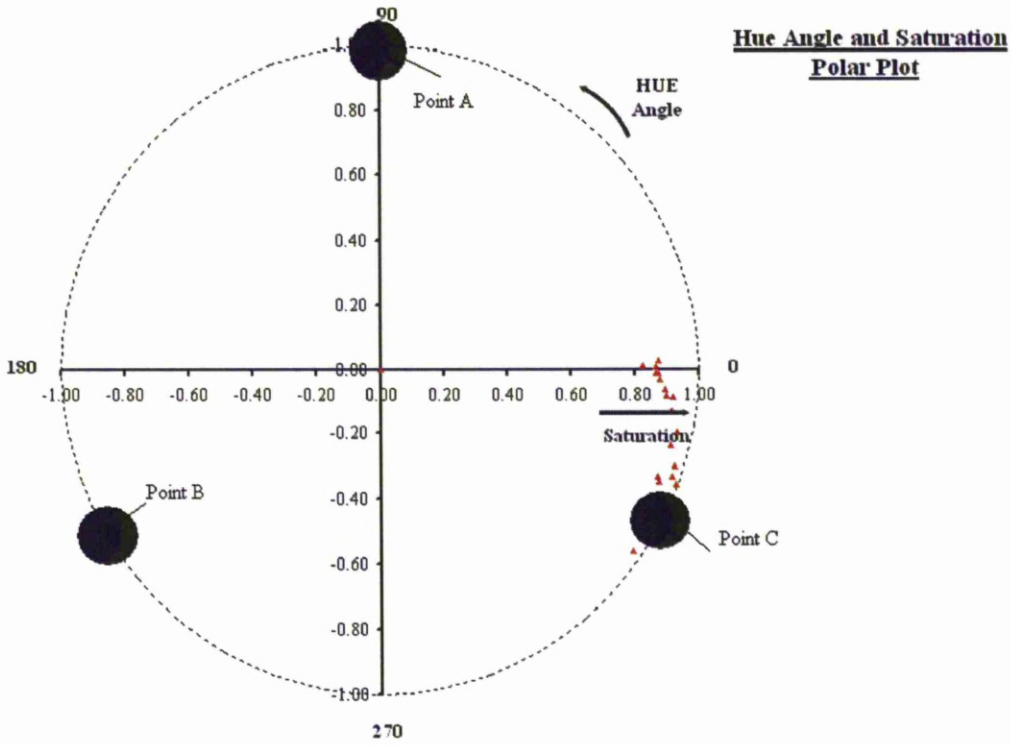


Figure 5-26: H-S Polar plot

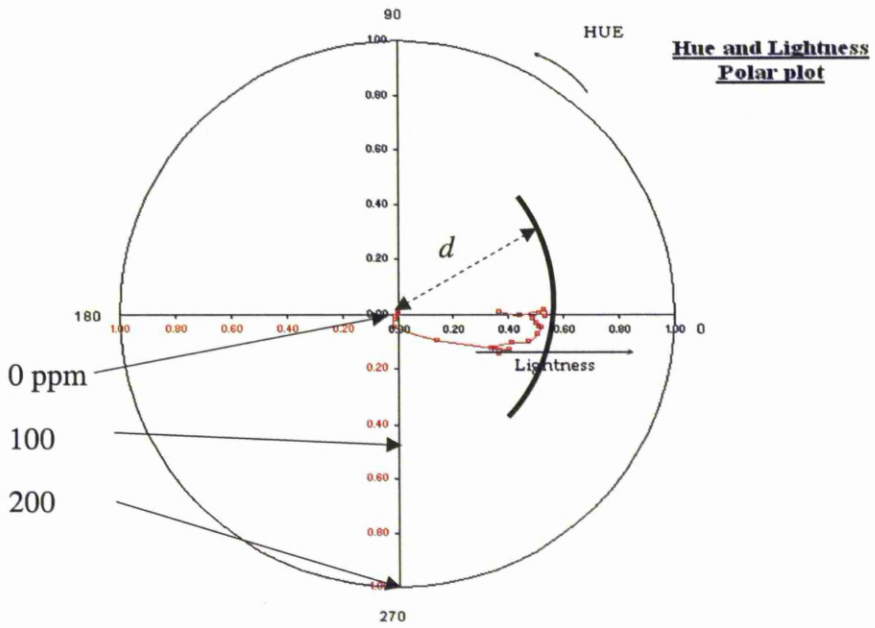


Figure 5-27: H-L Polar plot

As with the model tests, the H-S graph gives an indication of the position of the leak. The H-S graph shows that the data points are clustered together which is expected since the leak was close to the measurement point C in a similar way to the test in the last section when the CO_2 leak was positioned next to measurement point A. The H-L graph gives an indication of the concentration of SF_6 in air which from calibration is in the order of 100 PPM at the measurement point and is highlighted on the plot (*d*). Also since the graph is linear the scale can be used to indicate different concentrations of SF_6 in air. In the following sections is will be explained how to quantify the source concentration by estimating the diffusions coefficient by using calibrated sources.

5.5 The Three Dimensional Model

5.5.1 Introduction

In chapter 4 results were given in the form of mass spectrometer scans from 6 tri-stimulus measurement points that were positioned around the perimeter of a three dimensional space. Tests are performed using leaks at different points in the Sphere:

1. A small leak close to the centre of the 3D Space
2. A leak positioned next to one measurement point
3. A leak positioned in the bottom half of the of the 3D Space
4. A 200 ppm leak at the centre of the 3D space.

5.5.2 Dispersion Coefficient

As described in Chapter 2 it was shown that the source concentration of SF_6 can be estimated by using the following equation:

$$C = Qe^{-\frac{1}{2}\left(\frac{r^2}{d^2}\right)} \qquad \textbf{5-1}$$

To calculate the dispersion coefficient an SF_6 source with a concentration of 200PPM in air was positioned 0.5 M from the mass spectrometer. From

calibration the concentration measured at the mass spectrometer was calculated to be of 10 PPM. Using this information the dispersion coefficient for this system with SF_6 is:

$$d = \sqrt{\frac{r^2}{-\left(2 \times \ln\left(C/Q\right)\right)}} = 0.204 \qquad \textbf{5-2}$$

This means that if the distance from the source is known and the concentration at that point is known then the source concentration can be calculated. However, the value for d is an approximate unit, for a more accurate result the environmental conditions would have to be much more controlled.

The mass spectra is subject to the same chromatic techniques discussed in the last section so that the SF_5^+ peaks are used to obtain HLS values. Since the results now consist of 6 values instead of three there are now two sets of H-L and H-S plots representing the horizontal and vertical axis.

5.5.3 Leak next to Measurement point Y

In Chapter 4 mass spectra were recorded when an SF_6 leak of 200PPM is released at measurement point Y, Figure 4-35, in the three dimensional space. This data is used to obtain HLS values which can be seen in the form of H-L & H-S plots in Figure 5-28 and Figure 5-29.

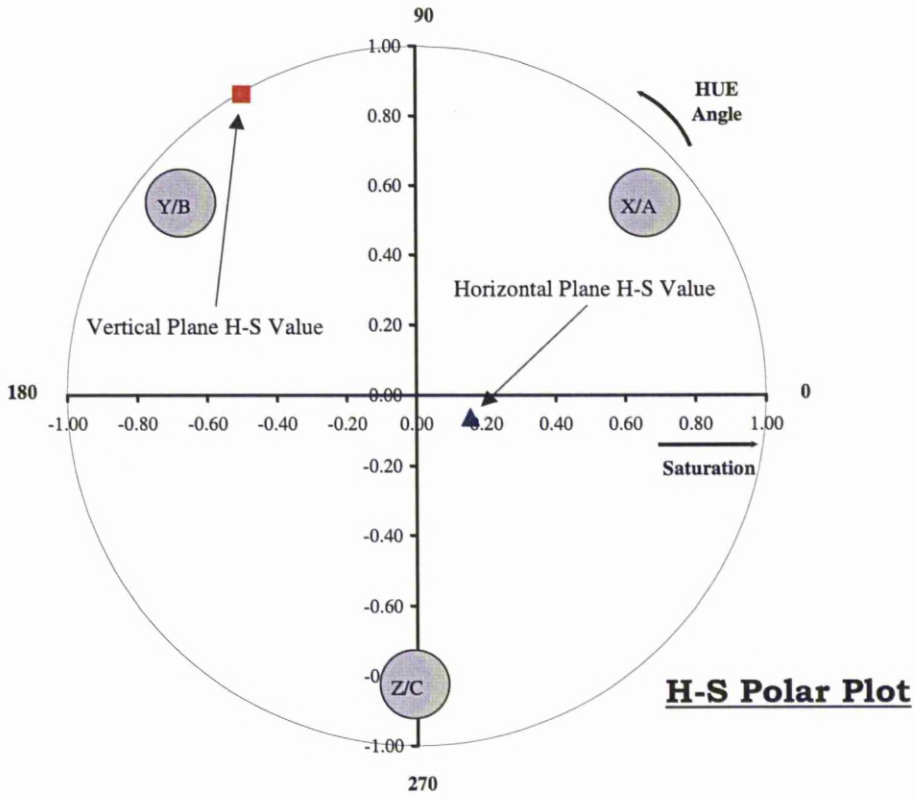


Figure 5-28: H-S for a Leak next to Y in the 3D Space

In the same way that the H-S plots for the CO_2 tests gave the physical position of the gas source the H-S plots here indicate the source of the SF_6 source. The blue triangle represents the position of the leak with respect to measurement points A, B & C (Horizontal plane) and the red square represents the position of the source of the gas with respect to measurement points X, Y & Z (Vertical Plane). It can be seen that the triangle is very close to the centre of the space and the square shows that the position of the leak is at measurement point Y.

Therefore it is possible by assessing both values to calculate that the source of the Leak is next to measurement point Y.

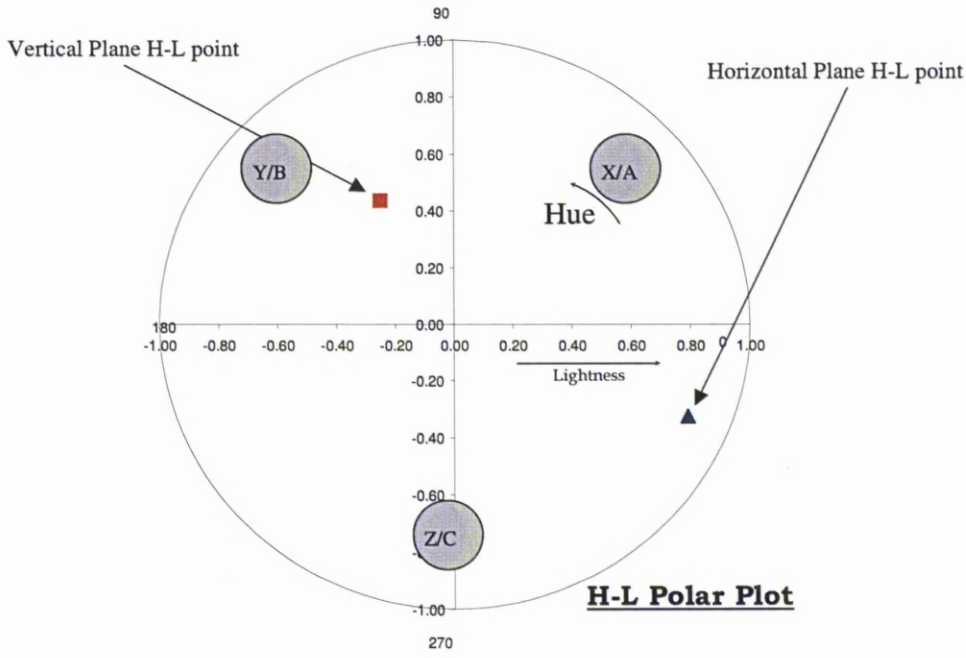


Figure 5-29: H-L for a Leak next to Y in the 3D Space

This H-L plot gives an indication of the dispersion between the three measurements points on each plane. The blue triangle is the H-L value obtained for the horizontal plane and the red square is the value obtained for the Vertical plane. The maximum peak that was recorded was in the region of 1 x 10^{-2} mBar which from calibration gives an indication of a concentration of 200 PPM in air and was only present at point Y which is equal to the concentration of the source.

The blue triangle is close to the edge of the plot because all of the mass spectra were similar (i.e. noise) and since there was no peak in any of the scans on the horizontal plane then dispersion appear be large. To get a better indication of dispersion then the signal to noise ratio has to be improved at each measurement point; however the H-S plot is largely unaffected. The noise level for these tests was quite high at 1 x 10^{-4} mBar equivalent to 1 PPM SF_6 in air.

5.5.4 Leak at the centre of the 3D Space of 200PPM

A leak is situated in the centre of the three dimensional system of 200PPM and left to migrate into the space. The mass spectra data is recorded and the HLS values are obtained which produces the following H-S and H-L plots:

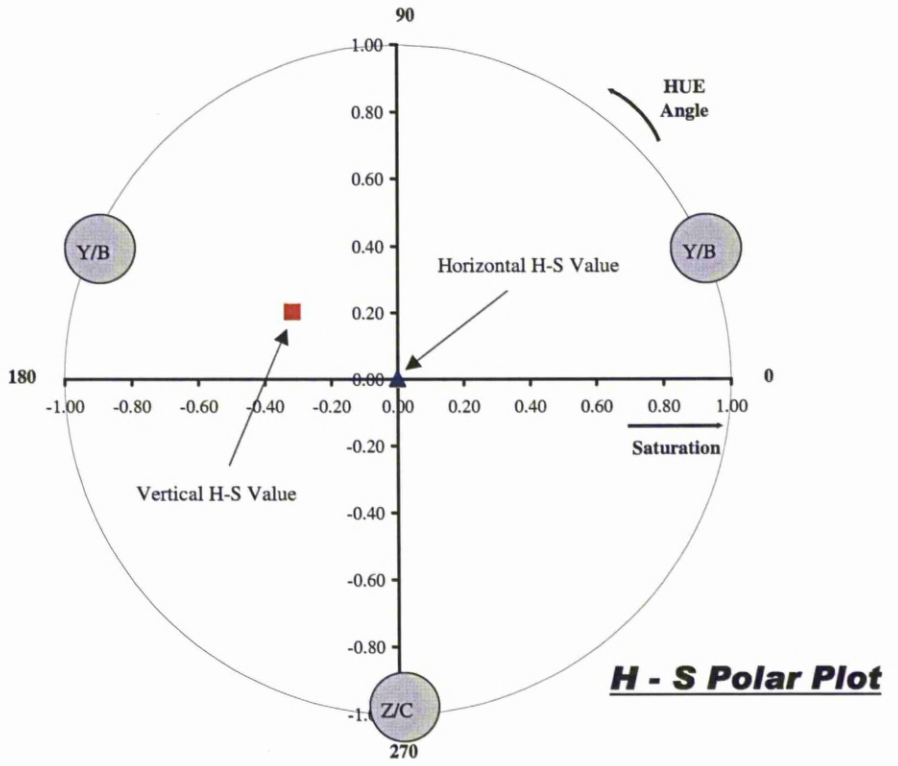


Figure 5-30: H-S for Leak at centre of 3D Space of 200PPM

The red square represents the vertical H-S value and the blue triangle represents the horizontal H-S value. The H-S plot indicates that the source of the gas is close to the centre of the Horizontal plane and a little towards point Y in the vertical. The drift in the vertical value is down to small air currents present during tests which affect the dispersion. The maximum SF_5^+ partial pressure peak at point C noted was approximately $1x10^{-4}$ mBar which from calibration indicates a concentration of 10 PPM SF_6 in air. Using equation 5-1 with a dispersion coefficient of 0.204, this indicates a source concentration of 200 PPM with the

source 0.5 M away. The maximum SF_5^+ peaks at the other points would have given the same result as the maximum peak values were the same.

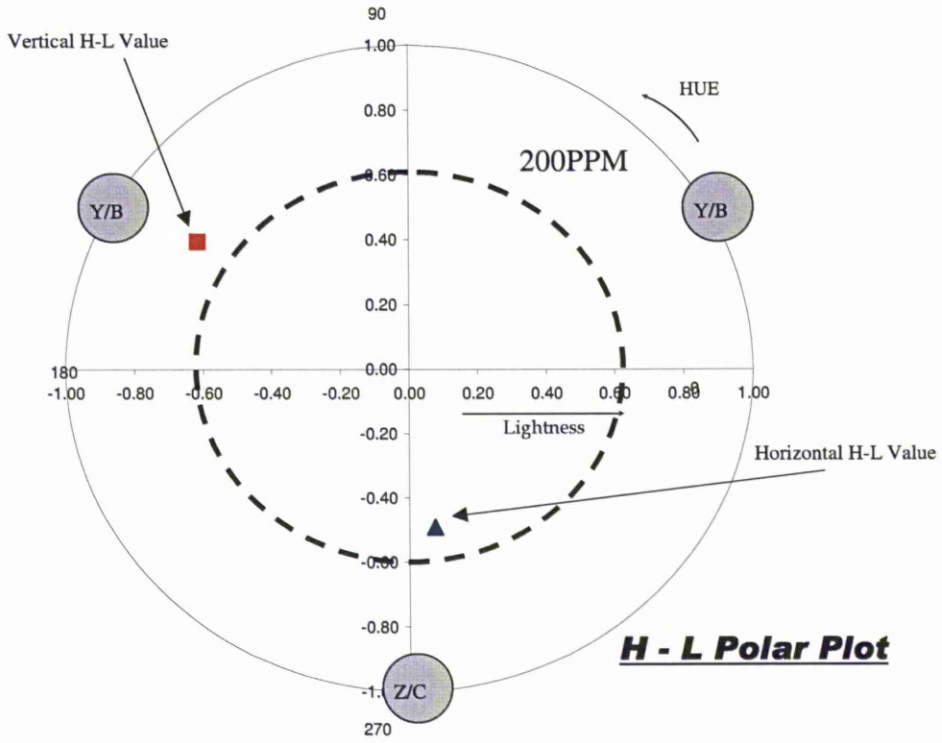


Figure 5-31: H-S for Leak at centre of 3D Space of 200PPM

The H-L Plot again gives and indication of source concentration and the two H-L values are in the same region where the dotted line represents 200PPM SF_6 in air. The plot is linear which means that the circumference of the plot (Lightness =1) represents approximately 333 PPM.

5.5.5 Small Leak in the Centre

The lowest concentration that was available to test with was 20PPM and therefore in Chapter 4 tests were conducted to see of the three dimensional model was capable of detecting a 20 PPM leak from the centre of the space. The gas was left to disperse into the space and the mass spectra was recorded over 10 scans and hence the HLS data was obtained and the following figures give the resulting H-L and H-S plots.

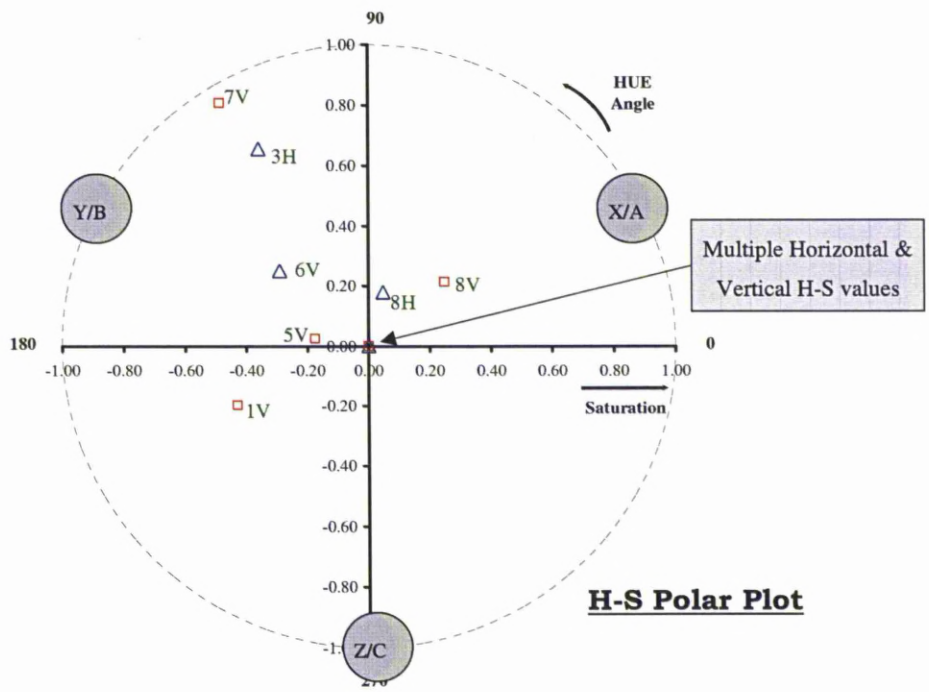


Figure 5-32: H-S for a Small Leak in the centre of the 3D Space.

The H-S values are label "*xH*" and "*xV*" where *x* is the scan number (1 to 10), *H* stands for Horizontal and *V* stands for Vertical. In theory the H-S values should all be the same because the gas has been allowed to disperse into the 3-dimensional space and the H-S plot should give an indication of the physical position of the gas source. There are many points at the centre that overlap which cannot be easily distinguished (i.e. Saturation & Lightness = 0). Although the majority of the H-S points are in the centre of the polar plot representing the leak position, many of the H-S values are sporadic. The reason for this is that the concentration at the source is very small and small drafts of air will have an affect on how the gas diffuses.

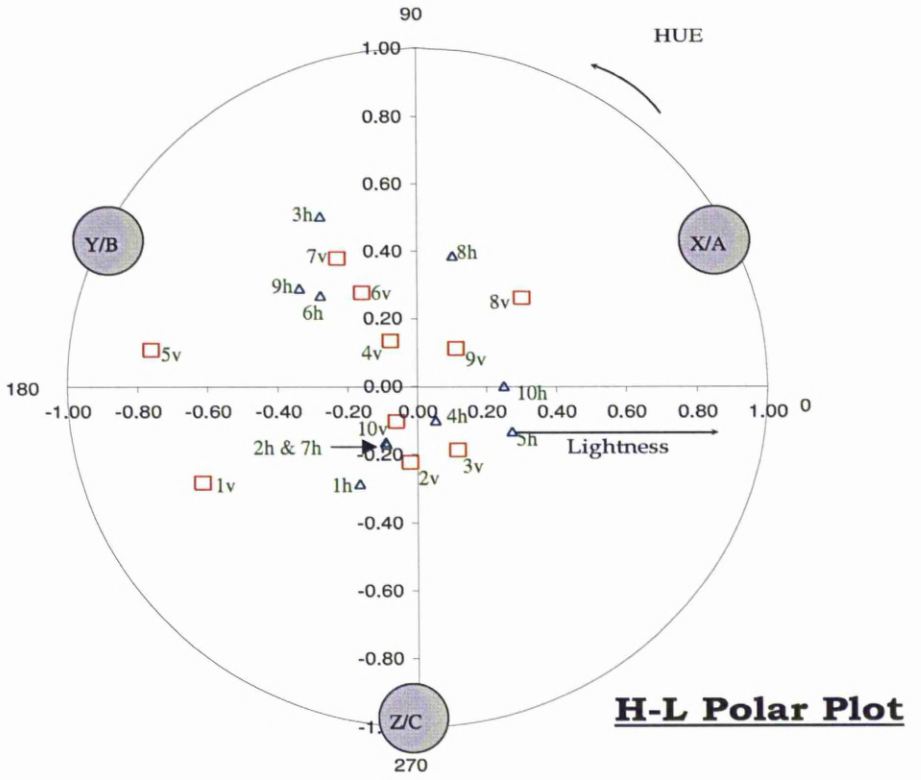


Figure 5-33: H-L for a Small Leak in the centre of the 3D Space

The values are marked "*xh*" or "*xv*" where x is the scan number (1 to 10) and the h stand for "horizontal" and v stands for "vertical". Like the H-S plot, the data in the H-L plot is difficult to decipher since the H-L data points appear to be random. The H-S plot produces a lot of similar values at the centre since it has been proven in the last set of tests that the H-S plot can still be useful at low signal to noise ratios. There were 10 mass spectra recorded at each point and a technique

used in chapter 4 to improve the signal to noise ration was employed to average the mass spectra together.

Averaging the first two scans together in order that single HLS values can be obtained produces the following H-L and H-S plots, Figure 5-34.

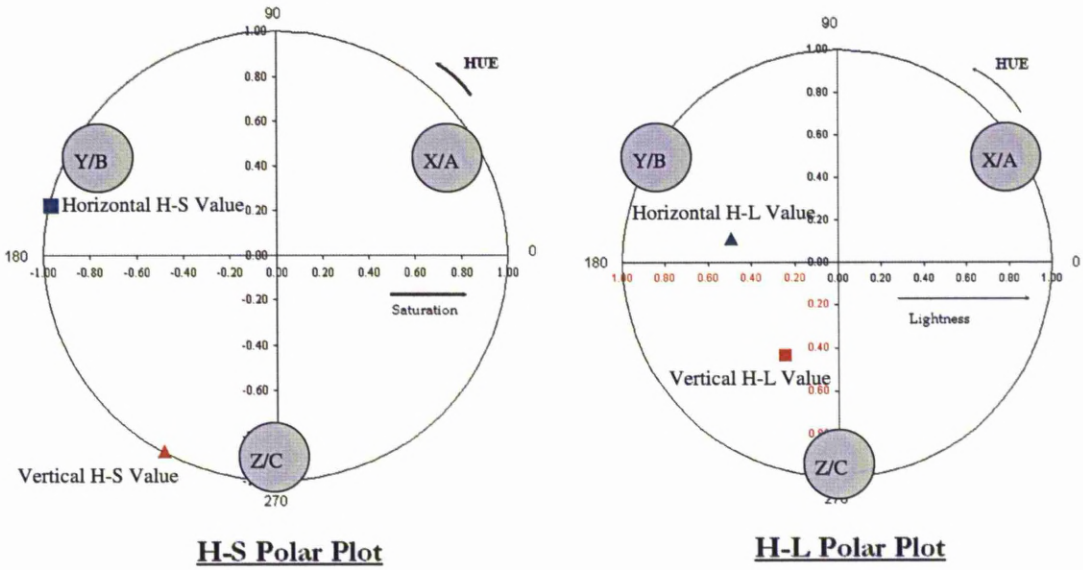
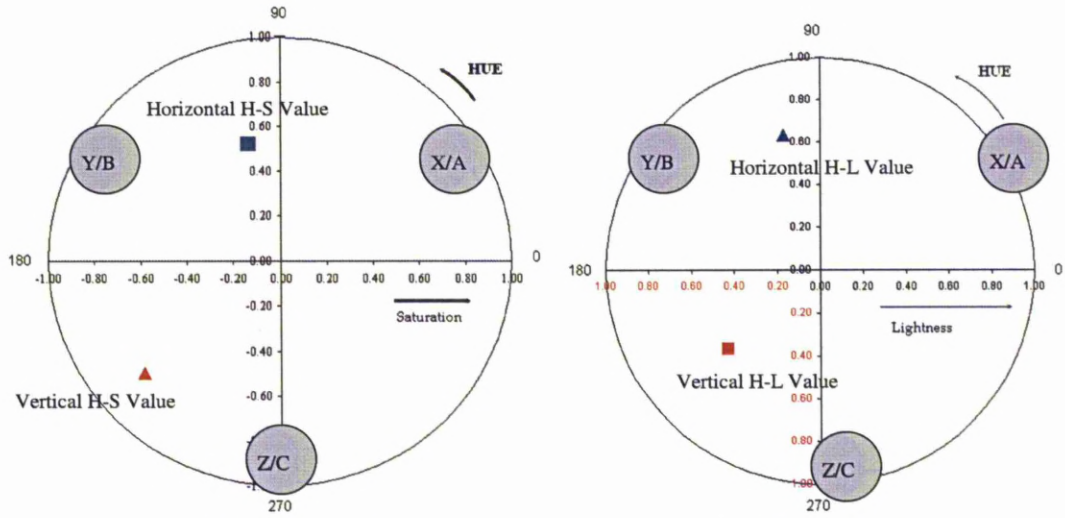


Figure 5-34: Small Leak at Centre Averaging 2 together

It can be seen that by averaging two scans together the physical position that the H-S plot indicates (near the bottom of the space close to point B) is not where the source was place. The Lightness values are at approximately the same value which is what should be expected as the source is at the same distance from each measurement point and therefore the concentration levels should be the same. However more scans must be considered.

The first five scans are averaged together and the HLS values are calculated to give the following H-L and H-S plots, Figure 5-35.



H-S Polar Plot **H-L Polar Plot**

Figure 5-35: Averaged Scans

Similarly as with averaging 2 scans together the H-S plot indicates the wrong position for the gas source although it can be seen that the H-S values have moved closer to the centre of the polar plot. The Lightness values are again the same indicating the same concentration.

Finally all 10 mass spectra are averaged together and the HLS values are calculated to give the following H-L and H-S plots.

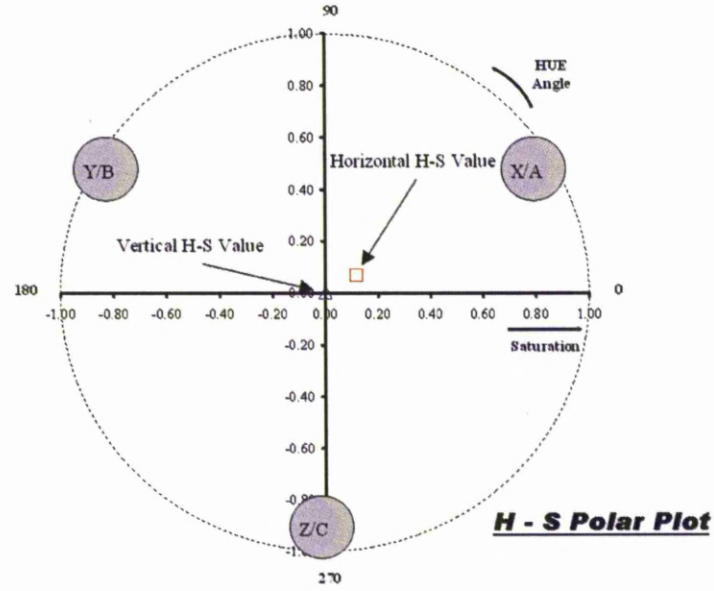


Figure 5-36: H-S plot after averaging the Scans

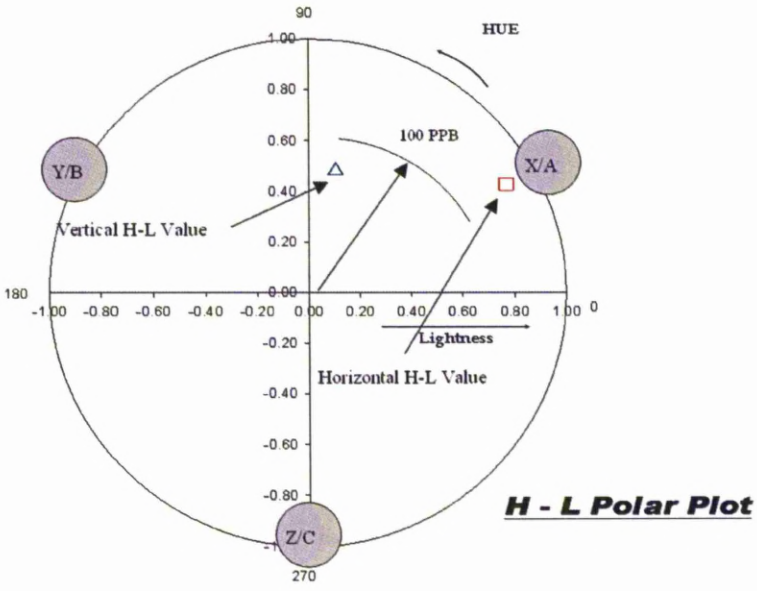


Figure 5-37: H-L after Averaging the Scans

It can be seen that the first two sets of polar plots in Figure 5-32 and Figure 5-33 were not sufficient to estimate source position and concentration. However, averaging 10 mass spectra together significantly improved the quality of the data which allowed the location and concentration at the source of the leak to be determined. Therefore it is important to average scans at low concentrations of SF_6 in order to improve data so that a reliable set of plots can be obtained.

A maximum SF_5^+ partial pressure peak of approximately 8 x 10^{-5} mBar was measured after averaging at measurement point A which implies that a concentration 0.8 PPM of SF_6 in air was present at this measurement point. Using equation 5-1 the source concentration is estimated to be approximately 16 PPM which is accurate to within 4 PPM of the calibrated sample. Since the H-L plot is linear the concentration of 100 PPB has been highlighted as the average of the two values.

5.5.6 Leak placed in the bottom half of the 3D space

In Chapter 4 mass spectra data was obtained in the three dimensional system with a leak positioned in the centre of the bottom half of the space with a concentration of 100 PPM. This data is used to obtain HLS data and Figure 5-38 and Figure 5-39 give the resulting H-S & H-L plots.

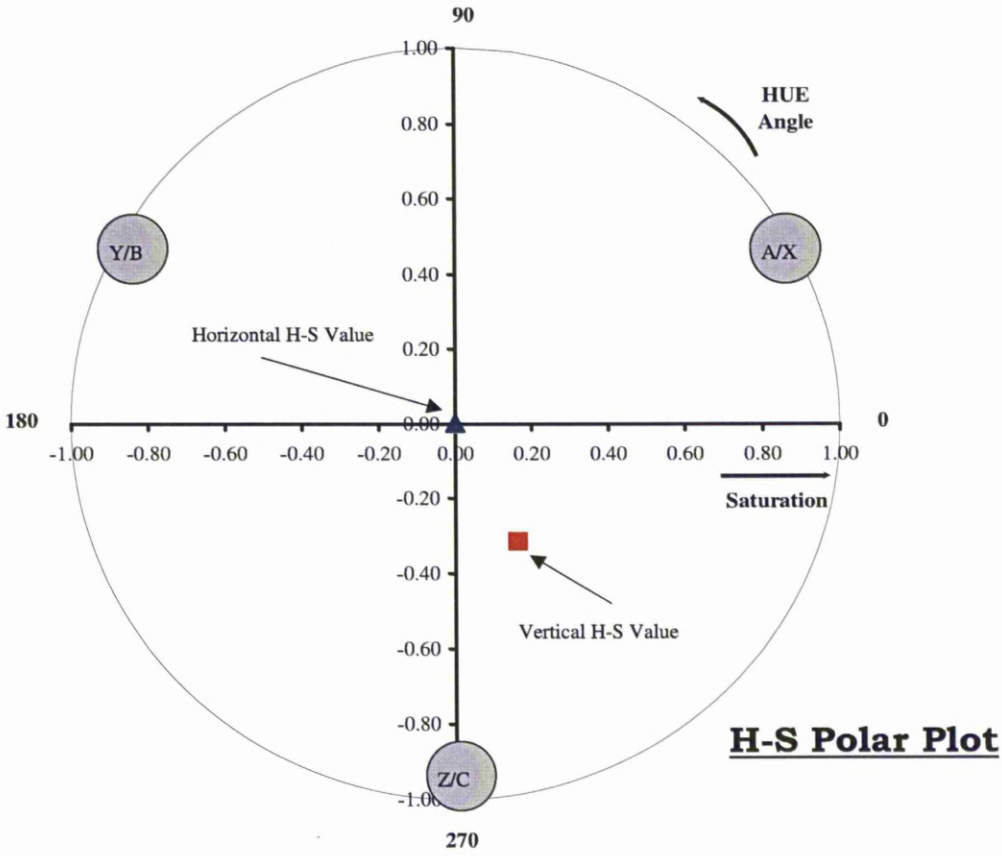


Figure 5-38: H-S for a Small Leak in the Bottom of the 3D Space

Observing the H-S plot, the blue triangle indicates the H-S value obtained for the horizontal plane and is in the centre of the plot as expected. The red square represents the H-S values obtained for the vertical plane and again as expected is in the bottom half of the polar plot.

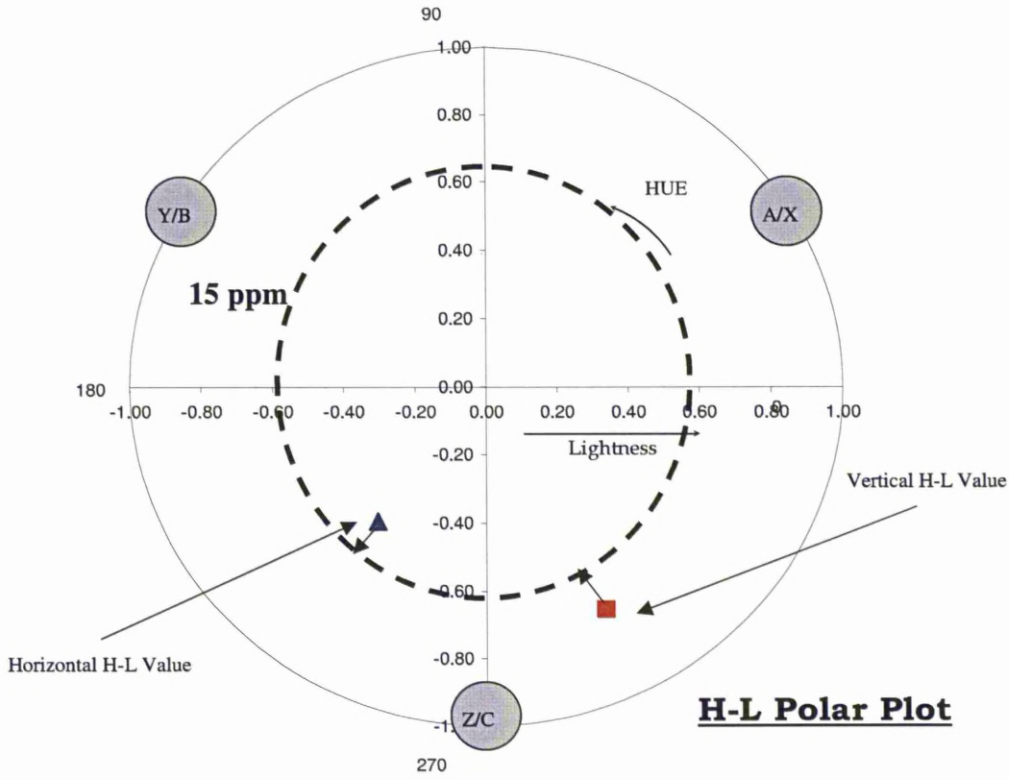


Figure 5-39 H-S for a Small Leak in the Bottom of the 3D Space

A maximum SF_5^+ partial pressure peak of $7x10^{-5}$ mBar was noted on the horizontal axis 0.5 M away from measurement point A. From calibration this pressure indicates a concentration of 700 PPB of SF_6 in air which suggests that at the source the leak consists of gas which has a concentration of 14 PPM SF_6 in air. This is within 6 PPM of the calibrated sample value. The dotted circle on the graph represents a boundary for this concentration. Ideally the two data points would sit at the same diameter however due to small air currents etc the dispersion

will be affected. Again the plot is linear which implies that the circumference for this H-L plot represents a concentration of SF_6 in air of 25 PPM.

5.5.7 Normalisation

The plots for each test describe above were obtained after normalising each set of scans to the highest peak obtained in that scan. The reason for normalising each set separately is that different concentrations of SF_6 in air give different SF_5^+ partial pressure peaks. For example if a set of scans with a maximum SF_5^+ partial pressure peak of 20 PPM was presented on a polar plot normalised to 500 PPM the values obtained would not give a visual indication of the source position on the polar plot. Therefore the data must be continually normalised. The following figures show the H-L and H-S plots that would be obtained if all of the tests were normalised to the highest peak noted throughout all of the tests. The highest peak noted was the peak at measurement point Y which gives a concentration level of 200 PPM.

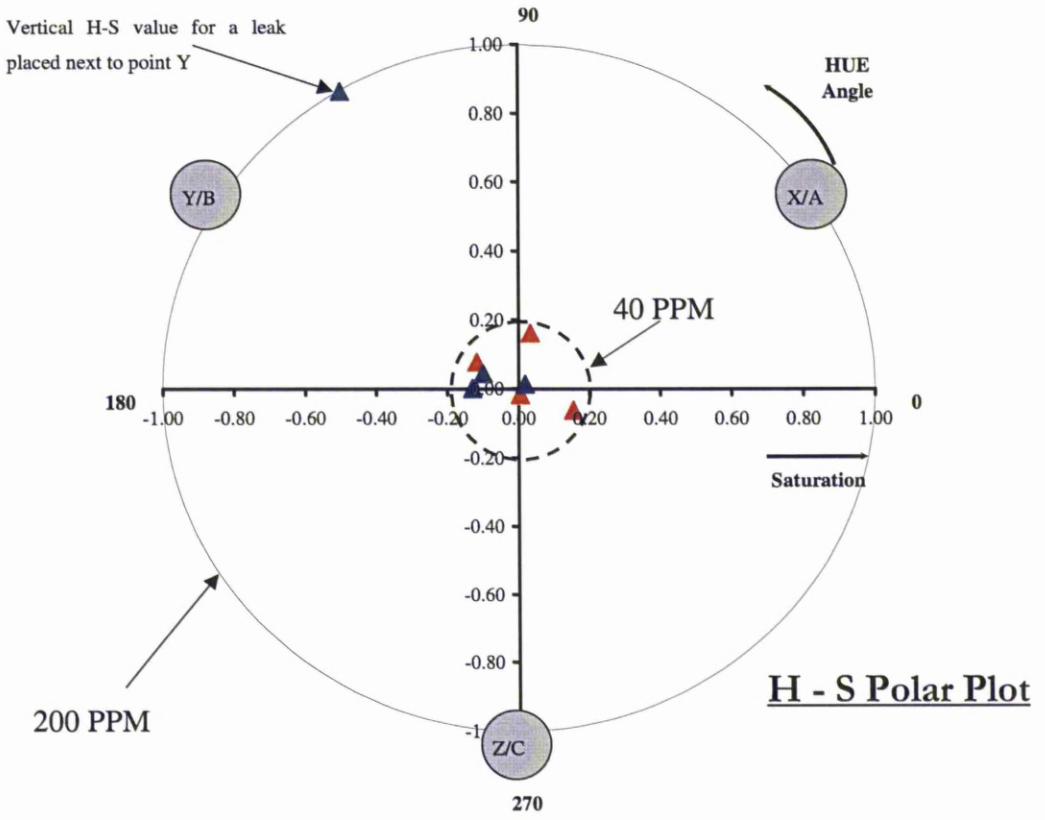


Figure 5-40: Hue & Saturation for 3D tests combined

The plots now become quite complicated and it becomes difficult to keep track of each point. The lone blue triangle at the circumference represents the vertical H-S value obtained when monitoring for a leak place next to measurement point Y. This was the largest of the leaks and hence it is at saturation of 1. However, the rest of the data points are all situated at the centre of the Polar plot within a small area an indication of position can not be determined.

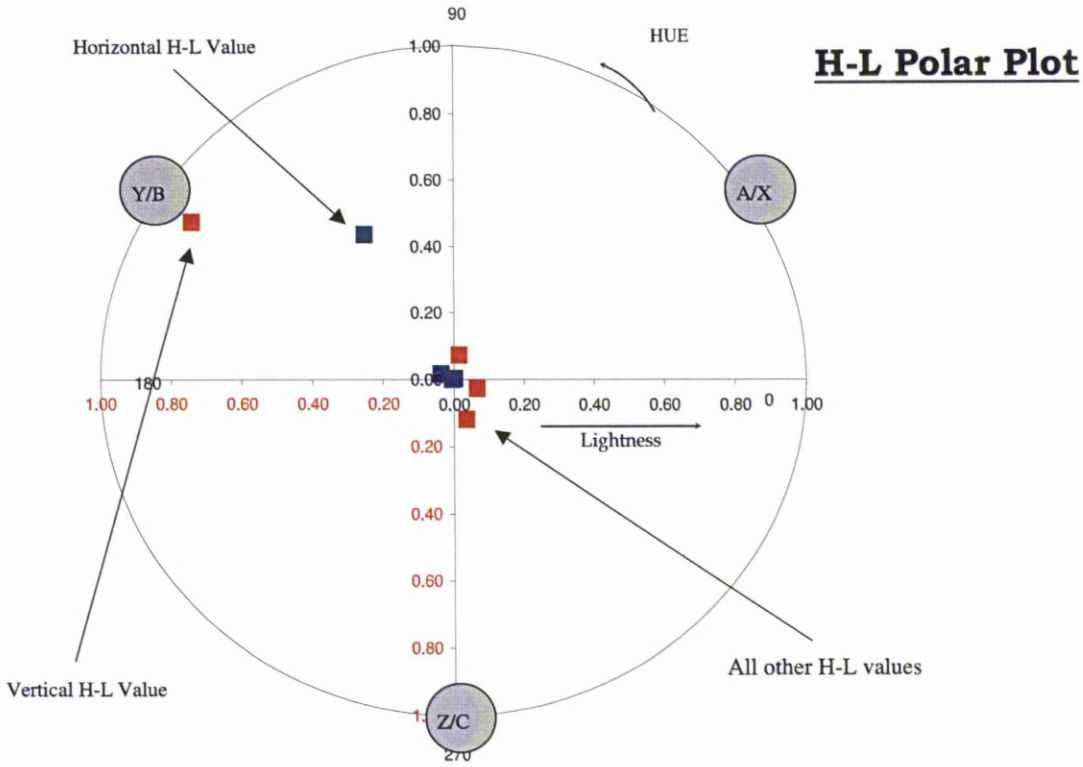


Figure 5-41: XYZ Plane Hue & Saturation for 3D tests

The H-L plot is supposed to give an indication of dispersion and leak size. The blue square is the Horizontal H-L value obtained when monitoring for a leak next to measurement point Y. The rest of blue squares representing the horizontal value for the other tests have now collapsed to the centre due to the large concentration dwarfing the other peaks. Likewise with the red square which is the vertical H-L value for the data taken when monitoring for a 200 PPM leak at the centre of the three dimensional space. The pressures measured in this test were

comparatively large compared to any of the other measurements taken in this plane in any of the other tests. For this reason the data points for the other tests have collapsed to the centre of the polar plot.

5.6 Conclusion

5.6.1 Triangle Filters

A set of truncated Gaussian filters was applied to a mass range about the position of an SF_5^+ peak (127 AMU). The H-L plots that arise from shifting a truncated triangle filter along a scan show that a defined shape emerges when SF_6 is present. The shape will appear until the SF_5^+ partial pressure peak reduces to within the noise and then will collapse towards the centre. However, the shape appears when the signal could be mistaken for noise. Therefore, it may be possible to use this technique to identify emerging patterns in the mass spectra so that it is possible to monitor for lower concentrations of SF_6 in air than when using the mass spectrometer alone in the conventional mode. The H-S plots also present a defined shape and this shape may be used to give an indication of the amount noise for a particular scan. This technique could be used as a simple method of detecting peaks at any Atomic Mass over any mass range and could therefore be utilised in other applications, however, this is not within the scope of this project. Moving filters is good for low concentrations but difficult to interpret.

It has also been shown that by applying a fixed set of truncated triangular filters across a fixed mass range about an SF_5^+ will produce trends in the H-L and H-S plots. Furthermore, it has been proven that by monitoring the H-S & H-L plots together it is possible to check the position of the H-L and H-S values and quickly identify emerging patterns in the mass spectra that indicate the presence of SF_5^+ peaks and hence the presence of SF_6. It was demonstrated that SF_6 could be detected at a value within the noise of a partial pressure peak in the order of about 1×10^{-4} mBar which by calibration indicates a concentration of 1 PPM SF_6 in air. The highest peak which could be reliably determined visually on the mass spectra was by calibration a concentration of 5 PPM SF_6 in air. Therefore, it has been shown that this technique can be used to detect lower concentrations of SF_6 in air than can be detected by observing the Atomic mass range alone. It can also be seen that by monitoring the H-L plot it is possible to gain and indication of the concentration of SF_6 in the sample which is useful for determining position of leaks of a known size. Like the shifted triangle filter this method could also be applied over different mass ranges.

5.6.2 Two-Dimensional Tests

It has been shown that when SF_6 is present in a space, the application of using tri-stimulus measurement points and monitoring across a mass range for SF_5^+ partial pressure peaks can be used in order that HLS data can be obtained. It

has been shown that applying the chromatic technique to mass spectra data can provide an indication of leak position, its severity and the degree of dispersion. However, the detection system discussed in this section can only be utilised in two dimensions which would be useful over large areas where the height is insignificant compared to the area.

5.6.3 Three Dimensional Tests

It has been shown that using a 3 dimensional tri stimulus set up that the position of a leak can be obtained as long as there is a reasonable amount of data at each point. It can also be estimated what the concentration of SF_6 in air is at the gas source. This technique can be used when it know that there is an SF_6 leak present. It has been shown that it is important to continually normalise results in order the polar plots can be used to their full potential.

The tests have been conducted using low concentrations of SF_6 over short distances. It is impractical to perform tests using pure SF over large distances due to the cost of SF_6 and its harmful effects, however the results given in this project give a good indication that a monitoring system could be utilised over a large distance where higher concentrations of SF_6 are present such as that in power stations.

5.6.4 Limitations of System

The systems discussed have all been developed under stable conditions in the laboratory over relatively small areas. If a system was to be developed for use in open spaces over much larger areas then more factors would have to be taken into account such as strong winds, smaller concentrations of SF_6 in air. The systems developed also assume that there is just one leak. If multiple leaks were present with the chromatic space then a different approach may be required.

5.7 References

[1] Ellis Martyn Dean, *Non Intrusive passive acoustic monitoring of liquid flow systems,* Ph.D. Thesis, The University of Liverpool 2003, pg 3.27.

Chapter 6 – Conclusions and Further Work

6.1 Introduction

This Chapter draws together the conclusions of each section regarding the experimental results and analysis and presents them in the form of a general discussion looking at the different techniques that were utilised throughout this work. A Summary of the implications of the analysis presented in this thesis is given with suggestions of further research for the future.

6.2 General Conclusions

The experimental results presented in this thesis have shown that it may be possible to monitor successfully for small or large concentrations of SF_6 in air using a combination of chromatic methods applied to mass spectra obtained from quadrupole mass spectrometers. The following sections give a general conclusion for each of the methods described in this project.

6.2.1 Determining concentrations of SF_6 in air

Laboratory tests and data collected onsite at KEMA in Holland presented in this thesis have proven that by monitoring the SF_5^+ peak at 127 AMU using a quadrupole mass spectrometer, it is possible that the concentration of SF_6 in air can be determined by using Calibration data and simple equations. This has been shown using mass spectra data taken from two quadrupole mass spectrometers manufactured by different companies. The calibration techniques used in this work give accurate results whether using a Faraday cup or whether using an electron multiplier in their sensitive modes of operation. Calibration must be performed regularly to achieve accurate results and are only valid for the same Mass spectrometer settings that they were recorded. Also, samples containing known concentrations of SF_6 in air are required in order to provide a linear graph that can be used to obtain a calibration equation.

6.2.2 Monitoring for small concentrations of SF_6

Results from Chapter 5 have shown truncated triangle filters taken from Chromatic methods can be applied to mass spectrometer scans in different ways. It has been shown that it is possible to provide a simple way of identifying emerging patterns in mass spectra in order that early detection of SF_6 may be

achieved by obtaining RGB and HLS values and then displaying data using H-S and H-L polar plots.

The methods of shifting a truncated triangle filter along an SF_5^+ peak and applying a fixed triangle filter were applied. It was shown that the H-S and H-L plots obtained can be used to give simple indications of whether or not SF_6 was present in a gas sample. These methods were shown to provide a fast and simple indication of SF_6 presence which was better than human interpretation of the raw Mass Spectra data.

It was shown that continual normalisation of filters is required to take full advantage of the capabilities of polar plots because of the linear characteristics of the polar plot. This technique could be used as a simple method of detecting peaks at any Atomic mass range and could therefore be utilised in other applications.

Other techniques have been used such as averaging scans together to improve the signal to noise ratio and eliminating negative pressure peaks in mass spectra scans. These techniques have also proven helpful when monitoring for small concentrations of SF_6 in air down to below 100 PPB.

6.2.3 Tri-Stimulus Measurement Points

Chapter 5 discussed the application of using tri-stimulus measurement points to obtain data. It was shown that by strategically positioning measurement points taken from Chromatic methods, it is possible to locate positions of single SF_6 leaks from equipment over relatively small areas. This was achieved by monitoring H-S and H-L plots in order to build up a physical profile of the position of a leak. It was also shown that it is possible to assess and estimate the concentration of SF_6 in air at the leak source within a tri-stimulus space by using Gaussian equations along with calibration results and knowledge of the 2-dimensional space.

This technique was proved successful in two dimensions and then also three dimensions. Over very large areas such as that in an electrical substation the two-dimensional system would be sufficient in order that a gas source and concentration can be estimated as the vertical height would be much smaller than the horizontal space. The three dimensional system provides much more information and would be useful in relatively small enclosed three dimensional spaces such as high power station units that are indoors or single circuit breaker units.

6.3 Further Work

There are a number of areas in which further work could be performed following on from this project. The following section describes some suggested further work.

6.3.1 Large Scale Testing

The results presented in this project have proved successful over relatively small areas using small concentrations of SF_6. Test over large scales using pure SF_6 were not possible due to environmental, personal safety and financial obstacles. The methodologies that have been developed within this project could be used to run long term tests onsite at a High Voltage Power Station.

Monitoring large areas using the tri-stimulus technique could be achieved using a quadrupole mass spectrometer. Longer tubes would be required to channel samples towards the mass spectrometer inlet. The following figure shows a simple method of positioning tri-stimulus measurement point within an enclosed area.

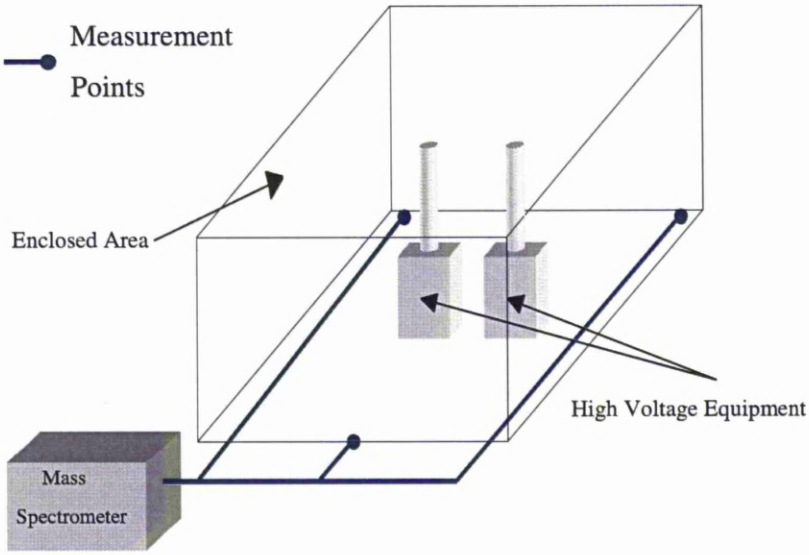


Figure 6-1: Laboratory set up

Great care would be needed on live equipment and for simplicity the two dimensional tests would be an ideal starting point in assessing the validity of using this system with pure SF_6 over large areas. As the tubes would be longer then data would need to be taken over long periods of time and continual averaging of results and normalisation would be required to improve signal to noise ratios and provide accurate H-L and H-S plots. A set of Calibration results would first be required for any system in order that concentrations of SF_6 in air can be successfully estimated. It would be advisable to repeat calibration tests at regular intervals since residual gas analyser results could drift over long periods of time due to instrumentation wear etc.

6.3.2 Monitoring for different gases

The methodologies contained in this project could be utilised over any mass range to monitor for different gases as proven when monitoring for CO_2 in chapter 5. These techniques could be used for monitoring and determining the location of other gas sources and their concentrations for example pollution monitoring. However, if the techniques were to be used over large areas outdoors then either the Eulerian or Lagrangian gas dispersion models described in chapter 3 would need to be considered.

6.3.3 Monitoring for lower concentrations

A residual gas analyser was used in the project and it was found that that using an electron multiplier rather than a faraday cup it was possible to detect smaller concentration of SF_6 in air. It could be possible to use other apparatus which would give more sensitive results such as a magnetic sector etc. to obtain mass spectra. The methods described throughout this project could be applied to this data in order that even smaller concentrations of gas can be detected. Tests were also subjected to small drafts in the laboratory which affected results. If the tests were performed in a completely stable environment then results would be more accurate.

6.3.4 Characterising gas samples using triangle filters

This project was concerned with only the gas Sulphurehexaflouride. The shapes that were described in Chapter 5 when applying shifted and fixed triangle filter were representative of a single SF_5^+ peak and were used to give an indication of SF_6 presence. If a larger mass range was investigated which contained more than one gas then the same techniques could be used to produce different shapes which could possibly be used produce information in the form of simple shapes to give an indication of the characteristics of a gas sample.

Appendix I

Papers related to work presented in this thesis

"Wide Area Substation Monitoring of SF_6 using mass spectrometry"

MC Kidman, A Pate, JW Spencer, GR Jones, JE Humphries

WIDE AREA SUBSTATION MONITORING OF SF6 USING MASS SPECTROMETRY

M. C. Kidman, A. Pate, J. W. Spencer, G.R. Jones, J. E. Humphries

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ABSTRACT

A quadrupole mass spectrometer (QMS) was used to detect SF_6. The mass spectrometer was calibrated using known concentrations of SF_6/air mixtures. Tests were undertaken involving an SF_6 gas kart, a circuit breaker when opened, SF_6 storage vessels and a known SF_6 leak at a substation. The spectrometer system used for these tests had no modifications to improve its performance but was capable of determining concentrations down to 45 part per million (PPM). This was the lowest concentration that was used for calibration purposes. Subsequent assessment of the noise level indicates that in its present unmodified state the system could detect approximately 10 PPM.

INTRODUCTION

Sulphurhexaflouride (SF_6) is used in gas insulation systems and both as an insulator and interruption medium in high power switchgear. The reason for the latter is that SF_6 provides and efficient arc-extinguishing medium and has excellent dielectric properties. Therefore, it can be assumed that SF_6 is going to be used for the foreseeable future. At present there are no alternatives to SF_6 that have the desired properties. However, SF_6 is known as one of the most potent greenhouse gases [1], which means that it is very important that this gas is handled with extreme care.

For the reasons mentioned above it is important that substations etc. are monitored to provide early warning of leakage. This paper gives an insight into a possible way of using a mass spectrometer to continually monitor for leaks in high power systems. Onsite tests were conducted at a sub-station to evaluate the validity of measuring small quantities of SF_6 and laboratory experiments are performed using a system designed to pinpoint leak position.

MASS-SPECTROMETER

The equipment that is used to monitor SF_6 is a residual gas analyser (RGA), which is a compact quadrupole mass spectrometer. Mass spectrometers are used to identify ionic species based on their charge to mass ratio (e/m). Very high levels of specificity and sensitivity can be obtained. Mass selection is performed by exerting a force on a charged particle moving through a magnetic field under high vacuum conditions. The particles are charged at an ion source and accelerated towards the analyser region and as they pass through the Quadrupole they are deflected according to their charge to mass ratio, figure 1.

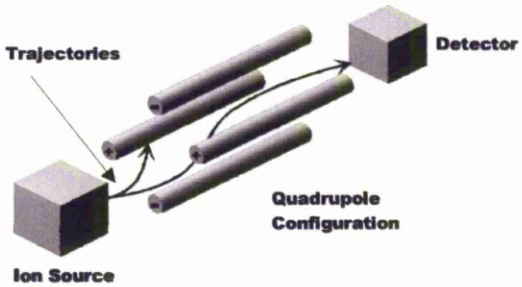


Figure 1: Quadrupole RGA

The output is qualified in atomic mass units (AMU) versus partial pressure and a typical ambient scan of air can be seen in figure 2.

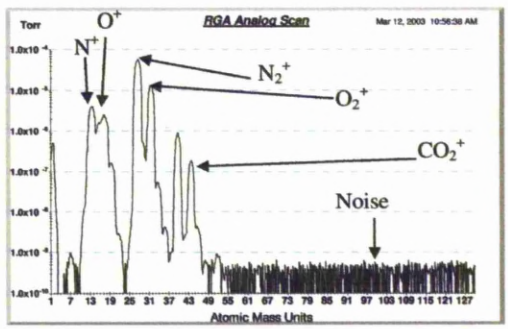


Figure 2: Typical ambient scan

The peaks in figure 2 are due to Helium, ionised species of air and water, N_2^+ and O_2^+. If measuring a gas in air the above peaks will always be present, therefore an ambient scan is taken before the sample is tested so that one can be subtracted from the other.

MEASURING SF_6 WITH AN RGA

When SF_6 is ionised in the RGA, the resulting gas is a combination SF_4^+, SF_3^+, SF_2^+, SF^+ and S^+ at masses 108, 89, 70, 51and 32 respectively. This is because the energy given to the SF_6 causes the molecule to fragment into smaller molecules. This fragmentation

of molecules occurs in most gases when they are subjected to measurement using mass spectroscopy and the fragmentation pattern is unique to each gas and is repeatable. The Mass spectrum produced by each gas is called its signature. The signature for SF_6 can be seen in figure 3.

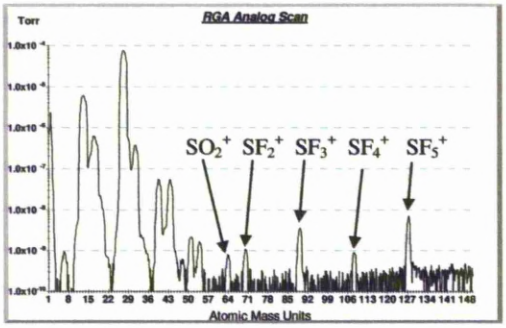


Figure 3: SF_6 signature

CALIBRATION

Flow gauges were used to obtain a number of samples of SF_6 diluted with air. The calibration samples obtained were of 45, 83, 168, 330 and 713 PPM were obtained. An RGA trace was obtained for each sample. Figure 4 shows the SF_5^+ partial pressure variations for given concentrations of SF_6 in air. The variation in partial pressure is due to the time taken for each peak to reach its maximum. Therefore, the maximum value recorded will be comparable to the concentration of the sample. This is verified by comparing the partial pressures of SF_5^+ and N_2^+.

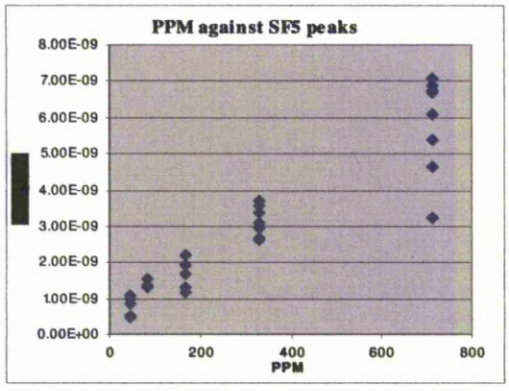


Figure 4: All SF_5^+ peaks against the concentration

Variations in the SF_4^+ and SF_3^+ peaks were also recorded, which also showed a similar trend to SF_5^+ but the proportional changes were not the same.

Figure 5 shows the sum of the SF_5^+, SF_4^+ and SF_3^+ peaks against PPM. The spread in values at each concentration is due to the transit time of the gas sample in figure 4.

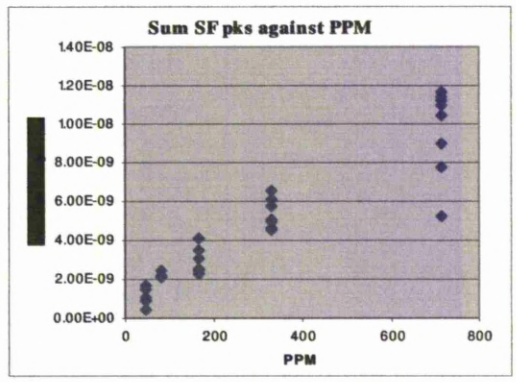


Figure 5: Sum of SF_5^+, SF_4^+ and SF_3^+ against PPM

Figure 6 shows the average and maximum SF_5^+ values plotted along with the average sum of the SF_5^+, SF_4^+ and SF_3^+ fragments and its maximum.

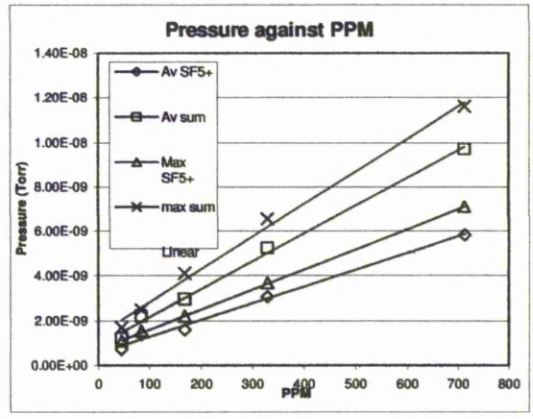


Figure 6: Averages and maximums against PPM

The graph shows a linear relationship between the amounts of SF_x detected expressed as partial pressure against concentration for the range of concentrations investigated. Although as expected, the summed components have a greater partial pressure, the gradients of SF_5^+ peaks and the gradients of the summed components are dissimilar. This implies that at higher concentrations of SF_6 in air a disproportionably higher amount of SF_3^+/SF_4^+ is produced, which can be seen by comparing the amplitudes of the peaks for SF_3^+ and SF_4^+ at different concentrations. The offset at 0 PPM is due to the noise in the detection system. Using the data in figure 6 for SF_5^+ the PPM of SF_6 can be found using the same system from (1):

$$PPM = \frac{SF_5^+ peak - 7\times10^{-10}}{9\times10^{-12}} \qquad (1)$$

ON-SITE TESTING

On-site tests were performed on switchgear units in a test bay and also at a substation. Two approaches were used to attempt to enhance the detection of SF_6 in air. The first method was to induce a positive flow of air towards the mass spectrometer. To assess the feasibility of this technique a pipe was inserted between a fan and the mass spectrometer 20 cm apart, figure 7.

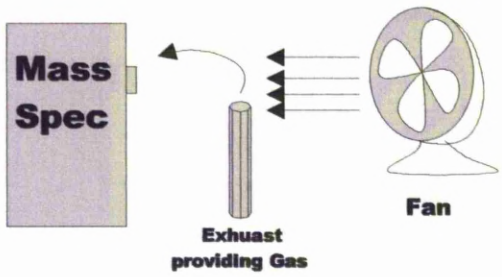


Figure 7: Test Set-up

Small amounts of SF_6 were released from the pipe. The maximum partial pressure recorded for SF_5^+ was 1.43×10^{-9} Torr, indicating a concentration of 81 PPM of SF_6.

The same method was used to take gas samples around an SF_6 storage vessel whilst it was being filled with SF_6. The maximum concentration detectable was at the limits of the resolution for this system, which was 7 PPM.

Further tests were undertaken during the opening of a circuit breaker, Figure 8.

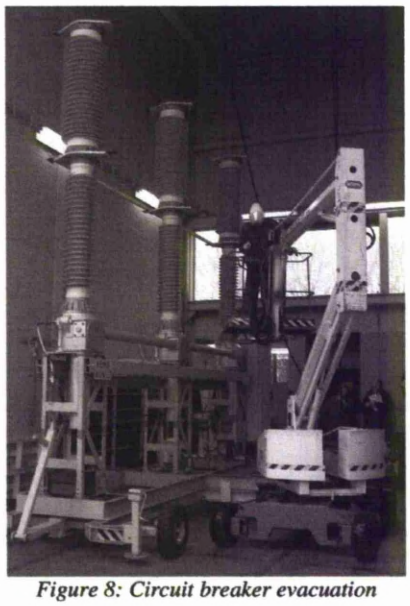


Figure 8: Circuit breaker evacuation

The SF_6 gas was first removed from the unit, which was then flushed with nitrogen (N_2). When the unit was opened the maximum concentration of SF_6 measured was 94 PPM even though the unit had been flushed with N_2. Tests at a substation were also undertaken but the collection method altered in order to provide a more convenient deployment of the system. The new collection system was allowed an air sample to be drawn through a long tube connected to the mass spectrometer. Although the transit time was much longer, the system worked well enough to detect SF_6 emancipating from a leak within the 150 kV substation. The concentrations measured at the leak points were between 21 and 58 PPM.

DISCUSSION

The experiences arising from the above tests indicate that the collection of SF_6 is critical. Given the limitation of the present equipment, concentrations of down to 7 PPM were detectable. The deployment of the system for wide area monitoring is demonstrated by the tests undertaken at the substation. However, it is clear that there is a need to assess the location of multiple collection points similar to that used at the substation in order to detect possible leaks. The strategy therefore is to have one mass spectrometer connected to a series of inter connecting popes with assisted gas flow. Figure 9 shows the arrangement in the laboratory whose performance is being assessed between further site trials.

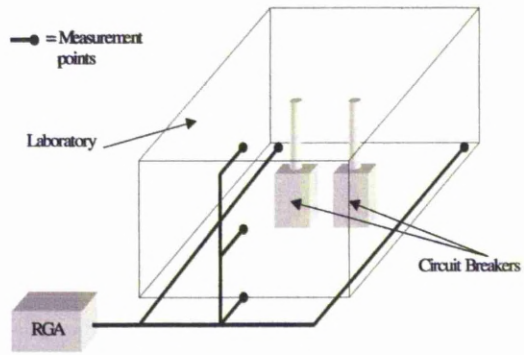


Figure 9: Laboratory Set up

CONCLUSION

The tests show that an unmodified mass spectrometer system was able to detect concentrations to 7 PPM. The calibration results show linear relationship with SF_6 concentrations. The tests proved the feasibility of using mass spectrometry for SF_6 leak detection. Improvements to the sampling system, to the mass spectrometer and the addition of an SF_6 concentrator

will help to increase the sensitivity of the system for detecting SF_6.

REFERENCES

[1] L. G. Christophorou, J. K. Olthoff, D. S. Green, Gases for Electrical Insulation and Arc Interruption: Possible Present and Future Alternatives to Pure SF_6, NIST Technical Note 1425, November 1997.

Appendix II

The following pages show the technical information regarding the equipment in this project:

Stanford Research Systems

RGA 100/200/300

MKS Instruments Inc.

CIRRUS™

Cole Parmer

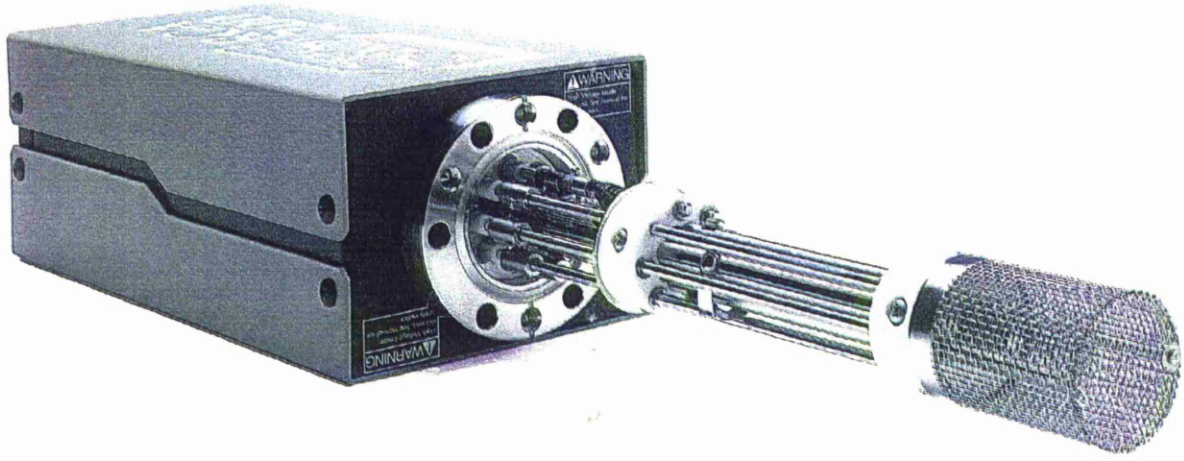
Mixing solenoid Valve & Tubing

Valco Instruments Co. Inc.

VICI 8-way Valve

Residual Gas Analyzers

RGA100/200/300 — 100 amu, 200 amu and 300 amu RGAs



SRS Residual Gas Analyzers

- **100, 200 and 300 amu systems**
- **Better than 1 amu resolution**
- **6 decades of dynamic range**
- **5×10^{-14} Torr detection limit**
- **RGA Windows & LabVIEW software**
- **Field-replaceable electron multiplier and filament**
- **RS-232 interface**

- **RGA100 ... $3750** *(U.S. list)*
- **RGA200 ... $4500** *(U.S. list)*
- **RGA300 ... $6000** *(U.S. list)*

The 100, 200 and 300 amu residual gas analyzers from SRS offer exceptional performance and value. These RGAs provide detailed gas analysis of vacuum systems at about half the price of competitive models. Each RGA system comes complete with a quadrupole probe, electronics control unit (ECU), and a real-time Windows software package that is used for data acquisition and analysis, as well as probe control.

Rugged Probe Design

The probe consists of an ionizer, quadrupole mass filter, and a detector. The simple design has a small number of parts which minimizes outgassing and reduces the chances of introducing impurities into your vacuum system. The probe assembly is rugged and mounts onto a standard 2.75" Conflat® flange. It is enclosed within a stainless steel tube, with the exception of the ionizer which requires just 2.5" of clearance in your vacuum system—about that of a standard ion gauge. The probe is designed using self-aligning parts so it can easily be reassembled after cleaning.

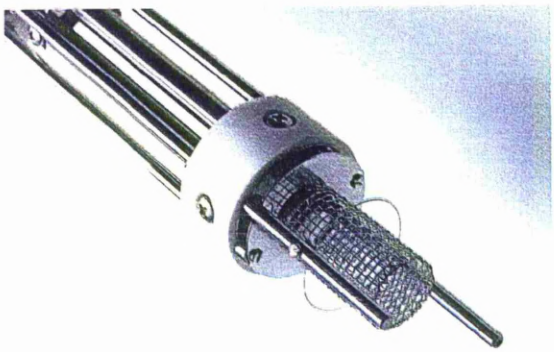
Compact Electronics Control Unit

The densely packed ECU contains all the necessary electronics for controlling the RGA head. It is powered by either an external +24 VDC (2.5 A) power supply or an optional, built-in power module which plugs into an AC outlet. LED indicators provide instant feedback on the status of the electron multiplier, filament, electronics system and the

probe. The ECU can easily be removed from the probe for high-temperature bakeouts.

Unique Filament Design

A long-life, dual thoriated-iridium (ThO_2/Ir) filament is used for electron emission. Dual ThO_2/Ir filaments last much longer than single filaments, maximizing the time between

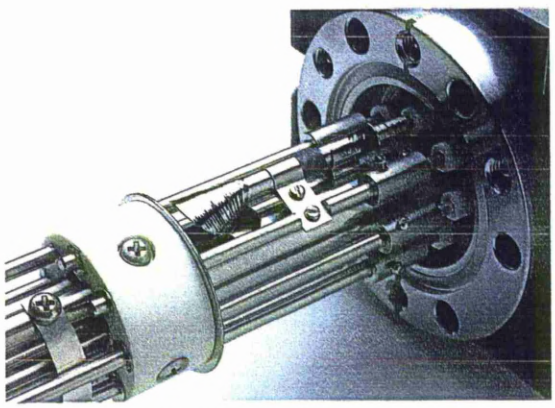


Dual ThO_2/Ir filament

filament replacement. Unlike other designs, SRS filaments can be replaced by the user in a matter of minutes.

Continuous Dynode Electron Multiplier

A Faraday cup detector is standard with all SRS RGAs, allowing partial pressure measurements from 10^{-5} Torr to 5×10^{-11} Torr. For increased sensitivity and faster scan



Continuous dynode electron multiplier

rates, an optional electron multiplier is offered that detects partial pressures down to 5×10^{-14} Torr. This state-of-the-art, multi-channel, continuous-dynode electron multiplier (EM) offers increased longevity and stability, and can also be replaced by the user—a first for RGAs.

Useful Features

SRS RGAs have a built-in degassing feature. Using electron impact desorption, the ion source is thoroughly cleaned, greatly reducing the ionizer's contribution to background noise.

A firmware driven filament protection feature constantly monitors (675 Hz) for over pressure. If over pressure is detected, the filament is immediately shut off, preserving its life.

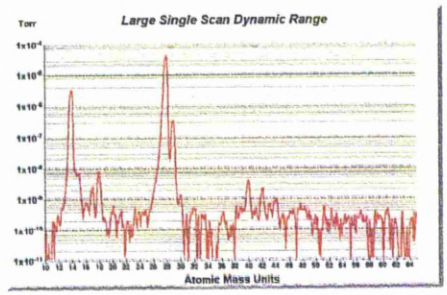
A unique temperature-compensated, logarithmic electrometer detects ion current from 10^{-7} to 10^{-15} amps in a single scan, with better than 2 % precision. This huge dynamic range means you can make measurements of small and large gas concentrations simultaneously.

Complete Programmability

Communication with computers is made via the RS-232 interface. Analog and histogram (bar) scans, leak detection, and probe parameters are all controlled and monitored through a high-level command set. This allows easy integration into existing programs.

RGA Windows Software

The RGA systems are supported with a real-time Windows software package that runs on PCs. The intuitive graphical user interface allows measurements to be made quickly and



RGA Windows software—Analog mode

easily. The program is fully interactive, giving the user complete control of the graphical display. Screens can be split for dual-mode operation, scales can be set to linear or log format, and data can be scaled manually or automatically. Data is captured and displayed in real time or scheduled for acquisition at a given time interval for long-term data logging. Features include user-selectable units (Torr, mbar, Pa and A), programmable audio and visual alarms, and comprehensive on-line help.

The software also allows complete RGA head control with easy mass scale tuning, sensitivity calibration, ionizer setup, and electron-multiplier gain adjustment. For further analysis, data files can be saved in ASCII format for easy transfer into spreadsheets. Graphic images can be saved as META files or copied to the clipboard for importing directly into other Windows programs. The software also provides password protection for locking out head parameters so that casual users can't alter important settings. A LabVIEW driver is also available on the SRS website.

An optional stand-alone monitor (PPM100) can be used to control the RGA without a host computer.

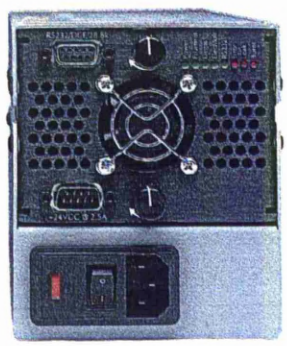
Multi-Head Operation

The software supports multiple head operation when more than one RGA is needed. Up to eight ECUs can be monitored from the software.

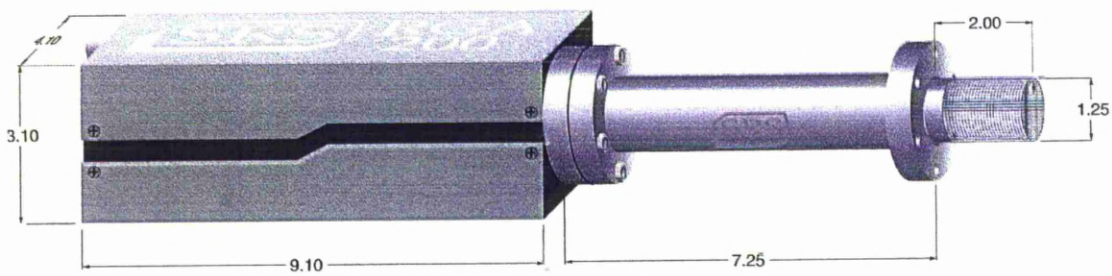
Performance and Value

The SRS family of RGAs is ideal for applications involving gas analysis, leak detection, and vacuum processing. We offer 100, 200 and 300 amu systems with supporting Windows software, and options that include an electron multiplier and a built-in power module for AC line operation. The RGA Windows software is available on the web at www.thinkSRS.com.

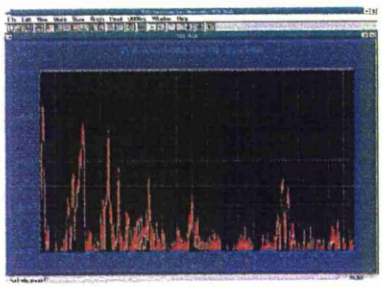
RGA rear panel (without AC power module)



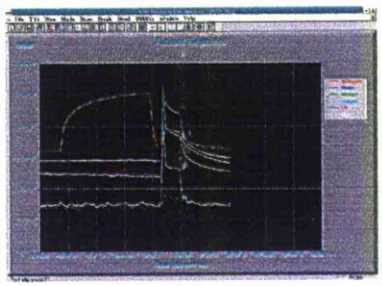
RGA rear panel (with AC power module)



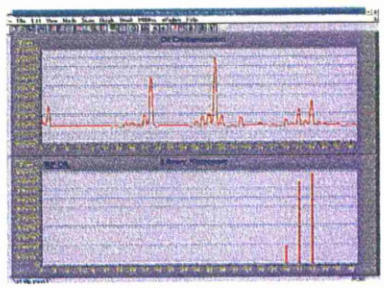
RGA dimensional drawing (inches)



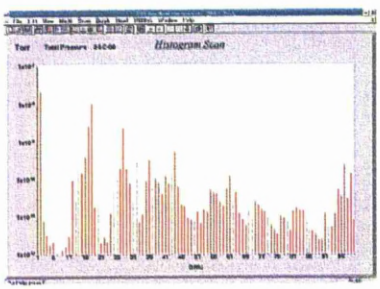
Analog mode provides a line graph representation of the acquired mass spectrum (partial pressure vs. mass number). Span, resolution and noise floor can each be set. Scans can be single-shot, timed or taken continuously.



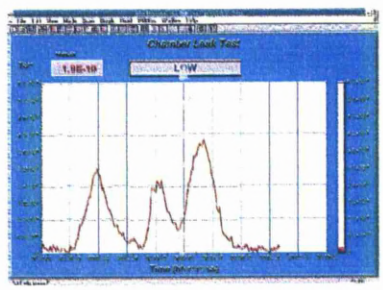
Pressure vs. time presents a strip chart of partial pressures for selected masses and provides a complete time history of your data. Complete scrolling and zoom control is available even while data is being acquired. This mode is most often used for monitoring process trends.



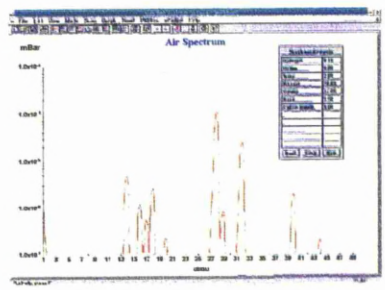
Library mode contains a comprehensive list of gases that can be used to compare against the current spectrum. A search mode allows you to select up to 12 masses and identify and display (numerically and graphically) the intensity of all gases that contain these masses.



Histogram mode displays a bar graph of partial pressure vs. mass, allowing the spectrum to easily be interpreted. This mode is often used for quick and easy vacuum analysis. The screen can be split for viewing two modes of operation simultaneously.



Leak detection mode monitors a particular mass number (not just helium) over time, and combines many features of the previous modes. A vertical bar graph provides a visual reference for viewing changes in intensity from a distance. A programmable audible tone, large numeric read-out, and visual alarm are also provided.



Analysis utility provides an approximation of the composition of gases being monitored by the RGA. Since more than one gas can contribute to a particular amu's partial pressure, the analysis mode is extremely useful in determining the make-up of complex gases. Up to 12 common gases can be selected for the analysis.

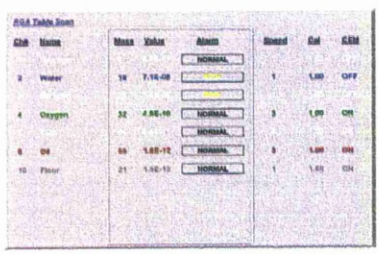
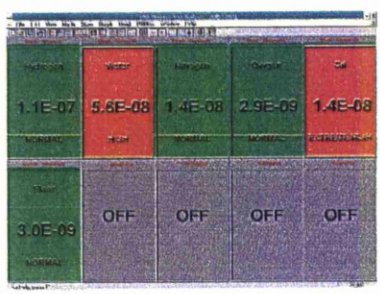
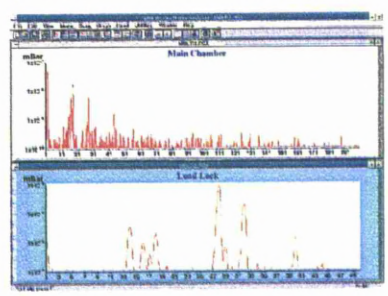


Table mode provides a readout of mass, scaling factor, and true partial pressure. The display shows the peak heights and alarm status of up to 10 masses. The electron multiplier can be independently set on or off for each mass. This allows the user to view minor species even in the presence of high total pressure.



Annunciator mode is provided for conveniently monitoring up to 10 masses. If a particular mass has tripped its preset alarm, the large box will turn red indicating a problem. An audible alarm will also be present until the mass falls back within its preset limits. This mode is most often used for Go/No-Go testing.



Multi-head operation is available when when more than one RGA is needed for analysis. Up to eight heads can be monitored simultaneously from the software.

Operational

Mass range	
RGA100	1 to 100 amu
RGA200	1 to 200 amu
RGA300	1 to 300 amu
Mass filter type	Quadrupole
Detector type	Faraday cup (FC), standard Electron multiplier (EM), optional
Resolution (per AVS std. 2.3)	Better than 0.5 amu @ 10 % peak height. Adjustable to constant peak width throughout the mass range.
Sensitivity (A/Torr)	2×10^{-4} (FC), <200 (EM). User adjustable throughout high voltage range. Measured with N_2 @ 28 amu with 1 amu full peak width, 10 % height, 70 eV electron energy, 12 eV ion energy, and 1 mA electron emission current.
Minimum detectable partial pressure	5×10^{-11} Torr (FC), 5×10^{-14} Torr (EM) Measured with N_2 @ 28 amu with 1 amu full peak width, 10 % height, 70 eV electron energy, 12 eV ion energy and 1 mA electron emission current.
Operating range	10^{-4} Torr to UHV (FC) 10^{-6} Torr to UHV (EM)
Operating temperature	70 °C (max.)
Bakeout temperature	300 °C (without ECU)

Ionizer

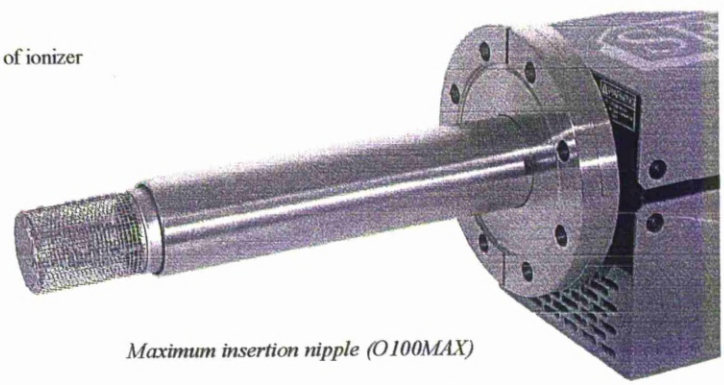
Design	Open ion source, cylindrical symmetry, electron impact ionization
Material	SS304 construction
Filament	Thoriated iridium (dual) with firmware protection. Built-in 1 to 10 W degas ramp-up. Field replaceable.
Electron energy	25 to 105 V, programmable
Ion energy	8 or 12 V, programmable
Focus voltage	0 to 150 V, programmable
Electron emission current	0 to 3.5 mA, programmable

General

Probe dimension	8.75" from flange face to top of ionizer
Probe insertion	2.0"
Probe mounting flange	2.75" CF
Minimum tube I.D.	1.375"
ECU dimensions	3.1" × 4.1" × 9.1" (WHD). Easily separated from the probe for bakeout.
LED indicators	Power ON/OFF, filament ON/OFF, degas ON/OFF, electron multiplier ON/OFF, RS-232 Busy, Error, Overpressure, Burnt Filament
Warm-up time	Mass stability ±0.1 amu after 30 minutes
Computer interface	RS-232C, 28,800 baud with high-level command set
Software	Windows based application
Power requirement	24 VDC @ 2.5 amps, male DB9 connector, optional built-in power module for AC line operation
Weight	6 lbs.
Warranty	One year parts and labor on defects in materials and workmanship

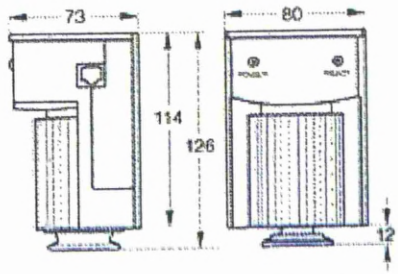
Ordering Information

RGA100	100 amu RGA w/ RS-232	$3750
RGA200	200 amu RGA w/ RS-232	$4500
RGA300	300 amu RGA w/ RS-232	$6000
Option 01	Electron multiplier	$1500
Option 02	AC power module	$250
Option 03	Ion counting output	$250
Option 04	NIST traceable 5 % calibration	$295
O100HJR	200 °C heater jacket	$395
O100MAX	Max. insertion nipple (4.5" CF)	$400
O100EM	Replacement electron multiplier	$1000
O100RF	Replacement ThO_2/Ir filament	$200
O100RI	Replacement ionizer kit (includes filament)	$450
PPM100	Optional stand-alone monitor	$2295



Maximum insertion nipple (O100MAX)

PENNINGVAC Transmitters PTR 225, PTR 225 S, PTR 237



Dimensional drawing for the PTR 225/225 S/237

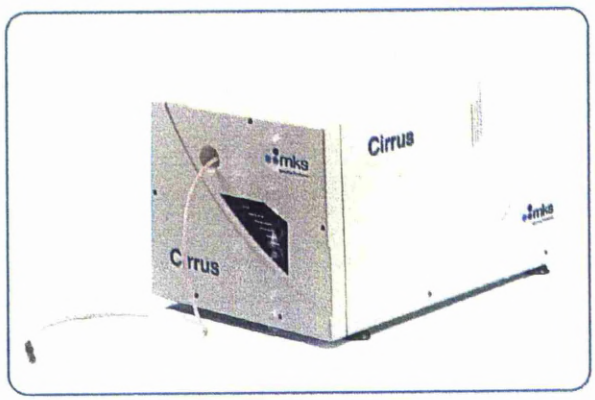
Technical Data		PTR Transmitter
Display range	mbar (Torr)	1×10^{-9} to 1×10^{-2} (0.75×10^{-9} to 0.75×10^{-2})
Measurement uncertainty		30 % in the range 1×10^{-8} to 1×10^{-4} mbar (0.75×10^{-8} to 0.75×10^{-4} Torr)
Principle of measurement		Cold cathode ionization after Penning
Supply voltage		14.5 to 36 V DC typ. 24 V DC hum voltage < 2 Vpp
Power consumption	VA	< 2
Storage/nominal temperature range	°C	-20 to +70/10 to 50
Max. rel. humidity (climatic-class F)	% n.c.	95
Protection class		IP 40
Dimensions (H x W x D)	mm	125 x 80 x 73
Weight, approx.	kg (lbs)	0.5 (1.1)
Inflammability		UL 94 - V 2
Sensor		Detachable for cleaning
Vacuum connection	DN	25 KF or 40 CF
Degassing temperature, max.	°C	350 with electronics detached
Dead volume, max.	cm^3	21
Materials in contact with the medium		Stainless steel, CrNi, Al_2O_3 ceramics, NiFe, Mo, Cu, Ni, titanium
Over-pressure rating (abs.)	bar	10
Signal output (Ra > 10 kΩ)		0 to 10.6 V
Measurement signal		0.66 to 10 V, corresponds to 1×10^{-9} to 1×10^{-2} mbar logarithm. divisions 1.333 V/decade
Trigger (PTR 225 S)		Changeover relay contact

Adjustment range	mbar (Torr)	1×10^{-9} to 1×10^{-3} (0.75×10^{-9} to 0.75×10^{-3})
Hysteresis		about 30 % of the adjusted pressure
Rating		60 V, 0.5 A DC
Error status		Contact in its rest position when "no ignition" / "HT off"
High voltage control input		ON: At U < 2.9 V, or U > 12 V OFF: At U > 3 V, or U < 7 V
Status output		Voltage level
Ready to measure		HIGH (typ. 24 V DC)
Error (no ignition)		LOW (0 V)
Status indicators		Operation: Orange LED Ready to measure (ignited): Green LED Trigger (active): Green LED
Monitor output (Ra > 100 kΩ)		Jack socket (3.5 mm) at which the trigger setting is available
Electrical connection		FCC-68 socket, 8 way with shield
Cable length, max.	m	100
Interface		
PTR 225 PB		Profibus DP
PTR 237 D		DeviceNet

Ordering Information	PTR Transmitter
PTR 225, DN 25 KF	**Part No. 157 34**
PTR 225 S, DN 25 KF	**Part No. 164 34**
PTR 225 PB, DN 25 KF Profibus interface	**Part No. 896 41**
PTR 237, DN 40 CF	**Part No. 157 36**
PTR 237 D, DN 40 CF DeviceNet interface	**Part No. 896 42**
Replacement cathode plates, titanium (set of 5 pieces)	**Part No. 162 91**
Replacement anode ring	**Part No. 240 002**

Connecting cable, FCC 68 on both ends, 8 way with shield - Type A

5 m	**Part No. 124 26**
10 m	**Part No. 230 012**
15 m	**Part No. 124 27**
20 m	**Part No. 124 28**
30 m	**Part No. 124 29**
40 m	**Part No. 124 30**
50 m	**Part No. 124 31**
75 m	**Part No. 124 32**
100 m	**Part No. 124 33**



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Gas Analysis

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CIRRUS™

ATMOSPHERIC PRESSURE GAS MONITORING

Cirrus offers the versatility of state-of-the-art quadrupole mass spectrometry in a convenient bench-top configuration. Incorporating an ethernet interface, Cirrus systems may be operated from a local PC or connected directly into an ethernet network hub or switch for remote operation.

Cirrus systems are ideal for the on-line monitoring and analysis of gases and gas mixtures including trace contaminants in process gases; solvent vapors; hydrocarbons; atmospheric and inorganic gas species (including corrosives); freons and noble gases.

Gas compositions can be tracked over a wide dynamic range (ppb to percentage levels) with a speed of up to 150 data points per second. The heated silica capillary inlet ensures a rapid response to changes in gas composition.

Cirrus systems are manufactured from quality, field proven materials, which maximize reliability and uptime. The systems are easy to install and operate and features automatic start-up and shut-down routines as well as built-in vacuum and heater interlocking for system protection.

Particular consideration has been paid to ease of service and maintenance. Cirrus has been designed to allow easy access to the vacuum system, pump and inlet components for preventative maintenance and the replacement of consumable items (ion source filaments, capillary etc.).

Features & Benefits

- Monitors multiple gas species over a wide dynamic range of composition at atmospheric pressure
- Compact, modular design for ease of serviceability and maintenance
- Direct ethernet interface - fully network compatible
- Fast response, silica capillary inlet heated to 150°C
- Recipe driven Process Eye Professional™ software for automated operation and calibration

Application Examples

- Monitoring of trace contaminants in process gas
- Catalyst studies
- Fuel cell monitoring and development
- Heat treatment/furnace monitoring
- Membrane studies
- Glove box gas monitoring
- Lamp manufacture
- Gas supply monitoring (cylinder checks and special gas production)
- Freon detection and identification
- Environmental monitoring
- Thermal analysis - TGA, DTA
- Fermentation process monitoring

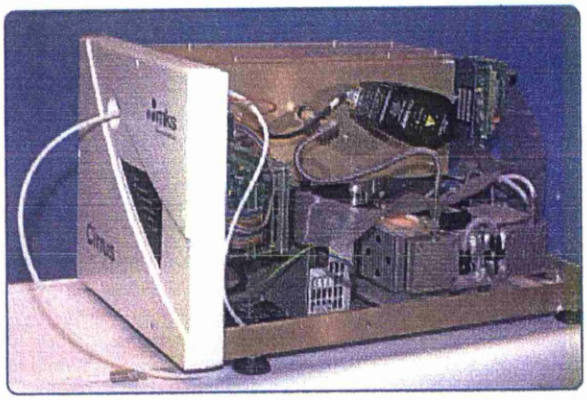
Cirrus Design Overview

Quadrupole mass spectrometers are now widely acknowledged as the preferred solution for many atmospheric pressure gas analysis requirements.They offer fast, on-line analysis with the ability to monitor a large number of different gases and gas mixtures with a single analyzer. Gas composition can be monitored over a wide dynamic range from ppb to percentage levels.

At the heart of every Cirrus system is a precision-built quadrupole analyzer incorporating a closed ion source, a triple mass filter and a dual (Faraday and Secondary Electron Multiplier) detector system. This analyzer configuration is selected to optimize sensitivity and long-term stability performance.

The Cirrus analyzer operates inside a stainless steel vacuum chamber, which is pumped by an oil free high compression turbomolecular/diaphragm pump combination. The whole vacuum chamber and inlet interface assembly is housed inside an oven with a radiant heater. The oven may be used to raise the temperature of these components during analysis, thereby preventing sample vapor condensation. Alternatively, the entire Cirrus vacuum chamber can be baked to reduce residual gas background species and to minimize any memory effects.

The Cirrus internal oven has a removable cover allowing easy access to the inlet interface, vacuum chamber and analyzer ion source. This is particularly helpful for routine maintenance like filament and capillary replacement. A cold cathode gauge is incorporated for independent vacuum pressure measurement and to provide an interlock signal for protection of the mass spectrometer. A temperature sensor also ensures that the electron multiplier detector cannot be switched on at high temperatures. The Cirrus is designed with a lubricant free pumping system and no elastomer seals used in the sample inlet system or in the high vacuum region of the system.



Internal View of the CIRRUS

Gas Inlet

An essential feature of any gas analyzer is that it should not contaminate or alter the gas sample in any way. The Cirrus inlet assembly consists of an inert silica lined capillary, which can be heated to a constant temperature. The low volume and surface area of the assembly serves to maximize response speed while minimizing memory effects. Cirrus systems can also be configured with inlets for multi-stream sampling.

Process Eye Professional™ - Cirrus Control Platform

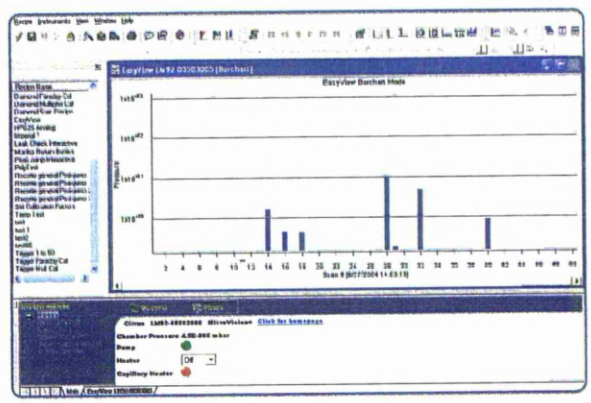
Cirrus is operated using Process Eye Professional software, a recipe-driven platform that communicates with the system over a TCP/IP network. Process Eye Professional is designed for use with the latest Microsoft® operating systems including Windows® XP and Windows XP Professional.

The features and benefits are as follows:

- Data presented in units relevant to the application
- Allows for fully automated operation and calibration
- User-configurable alarms and warnings
- Can be configured to track data from other process sensors (temperature, pressure, flow, etc.)

Cirrus Special Options

- Multi-stream inlet version (4 or 8 stream)
- Corrosive gas sample version
- Light gas pumping version (high compositions of H_2 or He)
- Regulated ion source pressure version for samples of varying pressure
- High mass resolution version



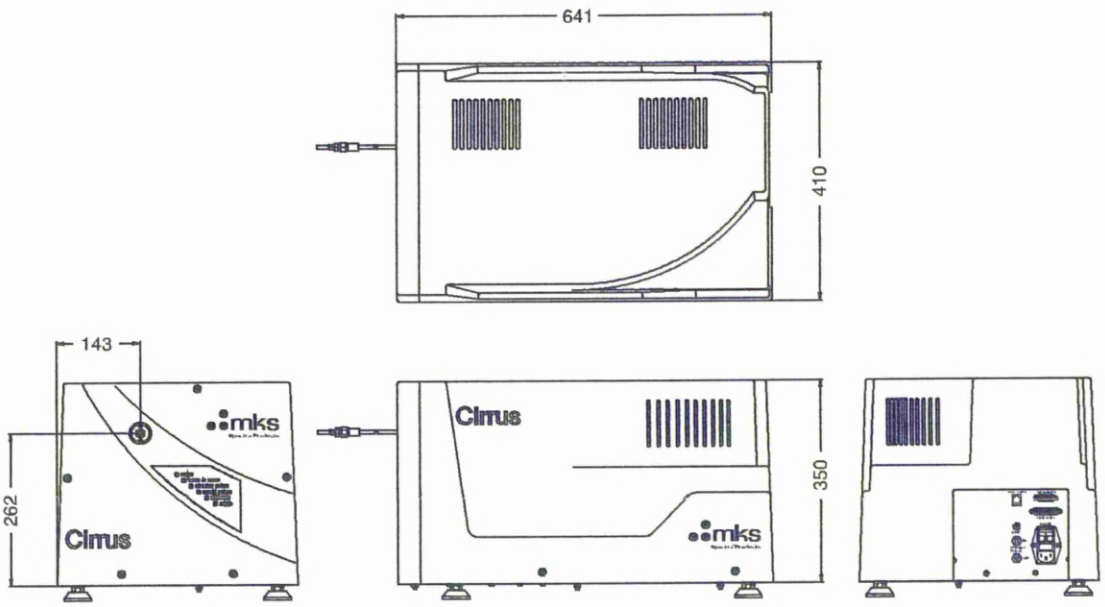
Software Display for Process Eye Professional™

Specifications

Dimensions & Weight	645mm L x 410mm W x 350mm H, 34.5 Kg
Electronics	1 – 200 and 1 – 300 amu standard 1 – 100 amu high performance optional
Detection Limits	Gas dependant, typically < 100 ppb for non-interfering species
Electron Energy & Emission Current	Operator variable
Maximum Operating Temperature (Turbo pump & electronics)	35°C, 80% RH (non-condensing)
Oven Temperature (Vacuum chamber & inlet interface)	180°C for bakeout, 80°C setting for operation at elevated temperatures
Capillary Inlet	2.0m long with ¼" Swagelok® end connection, heated to 150°C
Gas Consumption	20 ml/min
Sample Pressure	1 bar
Pumping System	High compression turbomolecular pump with internal 4-stage diaphragm backing pump standard
Recommended PC Spec	Pentium® IV or equivalent; Microsoft® Windows NT® 4.0, 98, Me, 2000, XP or XP Professional
Computer Interface	1 x LAN port required
I/O Capability (Cirrus-based)	3 analog inputs (0-10 volt, 16 bit) 1 analog output (0-10 volt, 16 bit) 12 TTL digital I/O (not if multi-stream inlet present)
Power	Universal mains input 90 – 264 VAC /44 – 66 Hz Maximum power consumption 800W (during bakeout)

Ordering Information

Product Ordering Codes:	Non-process	Process
	Cirrus (100 amu, non-process): 462-124-A30	Cirrus (100 amu, process): 462P-124-A30
	Cirrus (200 amu, non-process): 462-224-A30	Cirrus (200 amu, process): 462P-224-A30
	Cirrus (300 amu, non-process): 462-324-A30	Cirrus (300 amu, process): 462P-324-A30



Dimensional Drawing —

Note: Unless otherwise specified, dimensions are nominal values in mm.

mks
Technology for Productivity

Global Headquarters
90 Industrial Way
Wilmington, MA 01887-4610
Tel: 978.284.4000
Tel: 800.227.8766 (in USA)
Web: www.mksinst.com

MKS Gas Analysis
70 Rio Robles
San Jose, CA 95134
Tel: 408.750.0300

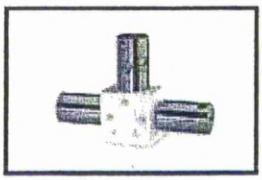
MKS Gas Analysis
Cowley Way
Crewe, Cheshire CW1 6AG
Tel: +44.1270.250150

Cirrus - 10/04

Product Detail Jump to category: Cole-Parmer Manifold Mixing Solenoid Valves

EW-01356-04 (3 of 24) [Previous | Next]

Cole-Parmer Manifold Mixing Solenoid Valves



click to enlarge

EW-01356-04
Cole-Parmer Manifold Mixing Solenoid Valve; 12 VDC, Teflon® body, 3 solenoid, 3 inlet, 1 outlet

Qty: 1 Add To Cart

£168.00 / each (GBP) Available in 7 days.

- Excellent for multiple liquid or gas control systems with aggressive or high-purity fluids
- Teflon® wetted parts
- Continuous duty and high cycle life
- Suitable for pressure or vacuum service

These normally closed solenoid mixing valves feature low power consumption, minimal dead volume, and fast response time for all your mixing needs. All valves come with 15" (26 gauge) Teflon coated lead wires. Special orders are available for valves with different diaphragm and body material, or larger flow values—call for more information.

Specifications

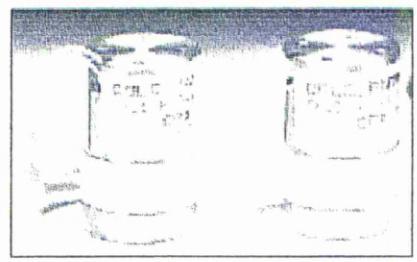
Max flow rate	14 LPM at 20 psi
Description	3 solenoid; 3-inlet, 1-outlet
Port size	1/4-28 UNF
Orifice	1/16"
Pressure range	Inlet port: 28" Hg to 20 psi Common port: 28" Hg to 35 psi
Max temperature	158°F (70°C)
Watts/solenoid	2.6
Power	12 VDC
Wetted materials	Teflon

Cole-Parmer 2- and 3-Way Direct Lift Solenoid Valves

Ideal for use with high-purity or corrosive fluids

Valves feature zero dead volume eliminating problems with trapped liquids. Rated for 26" Hg vacuum. Maximum fluid temperature is 158°F (70°C). All valves have 12" lead wires. All wetted parts are made of Teflon® PTFE.

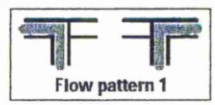
Valves are compact and lightweight—mount them almost anywhere. Mounting holes on both the top and bottom enable you to install valves in any position.



Two-way valve 01367-70

Two-way valve 98300-60

Three-way valve 98300-42



Flow pattern 1

Specifications & Ordering Information

Ports	Orifice	Max flow* at max psi	Max psi	Response time	Watts	12 VDC Cat. no.	12 VDC Price	24 VDC Cat. no.	24 VDC Price
Two-way normally closed valves									
¼-28	1/16"	16 L/min	30	15 msec	1.5	C-01367-70		C-01367-50	
¼-28	1/16"	45 L/min	100	20 msec	6.2	C-98300-60		C-98300-70	
¼-28	3/32"	31 L/min	30	20 msec	4.2	C-98300-00		C-98300-10	
1/8"†	5/32"	62 L/min	30	30 msec	7.2	C-98300-30		C-98300-40	
Two-way normally open valves									
¼-28	1/16"	16 L/min	30	15 msec	1.5	C-01367-71		C-01367-51	
¼-28	1/16"	45 L/min	100	20 msec	6.2	C-98300-61		C-98300-71	
¼-28	3/32"	31 L/min	30	20 msec	4.2	C-98300-01		C-98300-11	
1/8"†	5/32"	62 L/min	30	30 msec	7.2	C-98300-31		C-98300-41	
Three-way valves (follow flow pattern 1; see diagram at right)									
¼-28	1/16"	16 L/min	30	15 msec	1.5	C-01367-72		C-01367-52	
¼-28	1/16"	45 L/min	100	20 msec	6.2	C-98300-62		C-98300-72	
¼-28	3/32"	31 L/min	30	20 msec	4.2	C-98300-02		C-98300-12	
1/8"†	5/32"	62 L/min	30	30 msec	7.2	C-98300-32		C-98300-42	

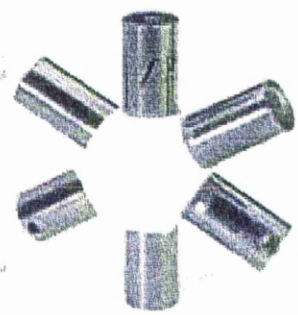
*Specified flow rates are for air. †NPT(F)

Cole-Parmer Manifold Mixing Solenoid Valves

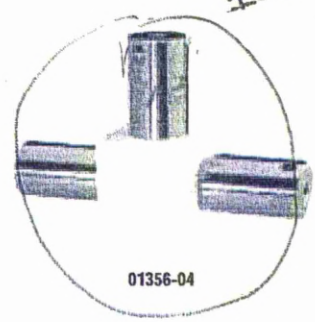
Excellent for multiple liquid or gas control systems with aggressive or high-purity fluids

- Teflon® or PEEK wetted parts
- Continuous duty and high cycle life
- Suitable for pressure or vacuum service

These normally closed solenoid mixing valves feature low power consumption, minimal dead volume, and fast response time for all your mixing needs. All valves come with 15" (26 gauge) Teflon-coated lead wires. Special orders are available for valves with different diaphragm and body materials, or larger flow values—call for more information.



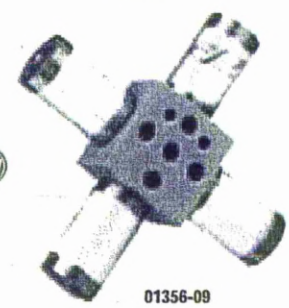
01356-16



01356-04

01356-00

New



01356-09

Specifications & Ordering Information

CE

Max temperature: 158°F (70°C)
Orifice: 1/16"
Watts/solenoid: 2.6
Max flow: 14 LPM at 20 psi

Ports: ¼-28 flat bottom
Pressure:
Inlet port: 28" Hg to 20 psi;
Outlet port: 28" Hg to 35 psi

Description	12 VDC Cat. no.	12 VDC Price	24 VDC Cat. no.	24 VDC Price
Teflon body valves				
2 solenoid, 2 inlet, 1 outlet	C-01356-00		C-01356-02	
3 solenoid, 3 inlet, 1 outlet	C-01356-04		C-01356-06	
4 solenoid, 4 inlet, 1 outlet	C-01356-08		C-01356-10	
5 solenoid, 5 inlet, 1 outlet	C-01356-12		C-01356-14	
6 solenoid, 6 inlet, 1 outlet	C-01356-16		C-01356-18	
8 solenoid, 8 inlet, 1 outlet	C-01356-20		C-01356-22	
PEEK body valves				
2 solenoid, 2 inlet, 1 outlet	C-01356-01		C-01356-03	
3 solenoid, 3 inlet, 1 outlet	C-01356-05		C-01356-07	
4 solenoid, 4 inlet, 1 outlet	C-01356-09		C-01356-11	
5 solenoid, 5 inlet, 1 outlet	C-01356-13		C-01356-15	
6 solenoid, 6 inlet, 1 outlet	C-01356-17		C-01356-19	
8 solenoid, 8 inlet, 1 outlet	C-01356-21		C-01356-23	

C-01356-50 **Mounting clip** for two-solenoid valve

CoolCube™ Circuit

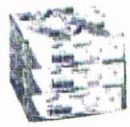
New

Preserve the life of your solenoid valves with this "hit and hold" circuit

Cat. no.	Dimensions	Price
SA-01356-51	1"W x 1"H x 9/32"D	

01356-51


Use barbed fittings with flexible tubing



BioPharm Platinum Silicone

See page 1910.

Formulation: Tygon® 3350 silicone, platinum-cured.

Applications: Pharmaceutical, cosmetic, industrial, and auto-analysis applications.

Characteristics: Ultra-smooth inner surface reduces particle entrapment and minimizes bacterial growth. Good for mild to medium concentration bases, salts, and alcohols; is odorless, tasteless, and non-toxic. Transparent.

Resin certification: Resin is FDA-compliant (21 CFR 177.2600); meets USP Class VI requirements, and NSF criteria. Tubing is manufactured according to GMP.

Temperature range: –112 to 392°F (–80 to 200°C)

Sterilize: With ethylene oxide, gamma irradiation, or autoclave for 30 min, 15 psi.

Catalog number	Dimensions, in. (mm) ID	OD	Wall	Max psi at 73°F	Price/ 50-ft pk
A-95702-00	1/32 (0.8)	3/32 (2.4)	1/32 (0.8)	16	
A-95702-01	1/16 (1.6)	1/8 (3.2)	1/32 (0.8)	10	
A-95702-02	1/16 (1.6)	3/16 (4.8)	1/16 (1.6)	15	
A-95702-03	3/32 (2.4)	5/32 (4.0)	1/32 (0.8)	7	
A-95702-04	3/32 (2.4)	7/32 (5.6)	1/16 (1.6)	12	
A-95702-05	1/8 (3.2)	3/16 (4.8)	1/32 (0.8)	7	
A-95702-06	1/8 (3.2)	1/4 (6.4)	1/16 (1.6)	9	
A-95702-08	3/16 (4.8)	1/4 (6.4)	1/32 (0.8)	5	
A-95702-09	3/16 (4.8)	5/16 (8.0)	1/16 (1.6)	7	
A-95702-10	3/16 (4.8)	3/8 (9.6)	3/32 (2.4)	9	
A-95702-13	1/4 (6.4)	3/8 (9.6)	1/16 (1.6)	5	
A-95702-14	1/4 (6.4)	7/16 (11.2)	3/32 (2.4)	7	
A-95702-16	5/16 (8.0)	7/16 (11.2)	1/16 (1.6)	5	
A-95702-17	5/16 (8.0)	1/2 (12.8)	3/32 (2.4)	6	
A-95702-18	3/8 (9.6)	1/2 (12.8)	1/16 (1.6)	4	
A-95702-19	3/8 (9.6)	9/16 (14.4)	3/32 (2.4)	5	
A-95702-20	3/8 (9.6)	5/8 (16.0)	1/8 (3.2)	7	
A-95702-25	1/2 (12.8)	3/4 (19.2)	1/8 (3.2)	5	
A-95702-27	5/8 (16.0)	7/8 (22.4)	1/8 (3.2)	4	
A-95702-28	3/4 (19.2)	1 (25.4)	1/8 (3.2)	4	

PharMed® Tubing

See page 1910.

Applications: Cell and tissue culture work and pharmaceutical uses. Also good for light-sensitive samples.

Characteristics: Nontoxic; nonhemolytic; extremely low permeability; resists acids, alkalies, oxidizing agents, and animal and vegetable oils; heat-sealable, bondable, and formable. Opaque beige.

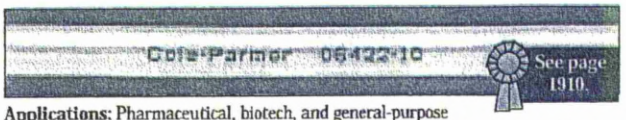
Resin certification: Resin is FDA-compliant (21 CFR 177.2600) and meets USP Class VI and NSF (Standard 51) requirements. Tubing is manufactured according to GMP.

Temperature range: –75 to 275°F (–59 to 135°C)

Sterilize: With autoclave, ethylene oxide, or gamma irradiation.

Catalog number	Dimensions, in. (mm) ID	OD	Wall	Max psi at 70°F	Price/ 25-ft pk
A-06484-00	1/50 (0.5)	9/64 (3.7)	1/16 (1.6)	50	
A-06484-02	1/32 (0.8)	5/32 (4.0)	1/16 (1.6)	40	
A-06484-04	1/16 (1.6)	3/16 (4.8)	1/16 (1.6)	34	
A-06484-06	1/8 (3.2)	1/4 (6.4)	1/16 (1.6)	19	
A-06484-08	3/16 (4.8)	5/16 (8.0)	1/16 (1.6)	13	
A-06484-10	1/4 (6.4)	3/8 (9.6)	1/16 (1.6)	10	
A-06484-12	1/4 (6.4)	1/2 (12.8)	1/8 (3.2)	19	
A-06484-14	5/16 (8.0)	7/16 (11.2)	1/16 (1.6)	8	
A-06484-16	3/8 (9.6)	5/8 (16.0)	1/8 (3.2)	13	
A-06484-18	1/2 (12.8)	3/4 (19.1)	1/8 (3.2)	11	
A-06484-20	5/8 (16.0)	7/8 (22.4)	1/8 (3.2)	8	
A-06484-22	3/4 (19.1)	1 (25.4)	1/8 (3.2)	7	

Clear C-FLEX® Tubing



See page 1910.

Applications: Pharmaceutical, biotech, and general-purpose lab uses requiring high performance. Economical alternative to platinum silicone.

Characteristics: Exceptional tensile and tear strength, good biocompatibility, excellent chemical resistance, low gas permeability, and a smooth surface. Transparent.

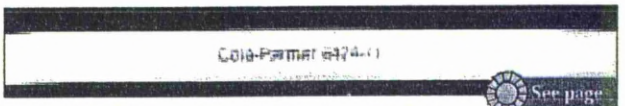
Resin certification: Resin meets USP Class VI and USDA requirements. Tubing is manufactured according to GMP.

Temperature range: –100 to 275°F (–73 to 135°C)

Sterilize: With autoclave, ethylene oxide, or gamma irradiation.

Catalog number	Dimensions, in. (mm) ID	OD	Wall	Max psi at 70°F	Price/ 25-ft pk
A-06422-00	1/50 (0.5)	1/12 (2.1)	1/32 (0.8)	50	
A-06422-01	1/32 (0.8)	3/32 (2.4)	1/32 (0.8)	51	
A-06422-02	1/16 (1.6)	1/8 (3.2)	1/32 (0.8)	25	
A-06422-03	3/32 (2.4)	5/32 (4.0)	1/32 (0.8)	23	
A-06422-04	1/8 (3.2)	3/16 (4.8)	1/32 (0.8)	17	
A-06422-05	1/8 (3.2)	1/4 (6.4)	1/16 (1.6)	35	
A-06422-06	5/32 (4.0)	7/32 (5.6)	1/32 (0.8)	17	
A-06422-07	3/16 (4.8)	1/4 (6.4)	1/32 (0.8)	15	
A-06422-08	3/16 (4.8)	5/16 (8.0)	1/16 (1.6)	22	
A-06422-09	3/16 (4.8)	7/16 (11.2)	1/8 (3.2)	36	
A-06422-10	1/4 (6.4)	3/8 (9.6)	1/16 (1.6)	20	
A-06422-11	1/4 (6.4)	7/16 (11.2)	3/32 (2.4)	28	
A-06422-12	1/4 (6.4)	1/2 (12.8)	1/8 (3.2)	28	
A-06422-13	5/16 (8.0)	7/16 (11.2)	1/16 (1.6)	17	
A-06422-14	5/16 (8.0)	1/2 (12.8)	3/32 (2.4)	27	
A-06422-15	3/8 (9.6)	1/2 (12.8)	1/16 (1.6)	17	
A-06422-16	3/8 (9.6)	5/8 (16.0)	1/8 (3.2)	23	
A-06422-17	1/2 (12.8)	11/16 (17.6)	3/32 (2.4)	17	
A-06422-18	1/2 (12.8)	3/4 (19.1)	1/8 (3.2)	17	

C-FLEX® Tubing



See page 1910.

Applications: Pharmaceutical, biotech, and general-purpose lab uses requiring high performance. Economical alternative to platinum-cured silicone tubing.

Characteristics: Exceptional tensile and tear strength, good biocompatibility, excellent chemical resistance, low gas permeability, and a smooth surface. Opaque white.

Resin certification: Resin meets USP Class VI and USDA requirements. Tubing is manufactured according to GMP.

Temperature range: –100 to 275°F (–73 to 135°C)

Sterilize: With autoclave, ethylene oxide, or gamma irradiation.

Catalog number	Dimensions, in. (mm) ID	OD	Wall	Max psi at 70°F	Price/ 25-ft pk
A-06424-59	1/50 (0.5)	1/12 (2.1)	1/32 (0.8)	30	
A-06424-60	1/32 (0.8)	3/32 (2.4)	1/32 (0.8)	31	
A-06424-62	1/16 (1.6)	1/8 (3.2)	1/32 (0.8)	15	
A-06424-63	3/32 (2.4)	5/32 (4.0)	1/32 (0.8)	14	
A-06424-64	1/8 (3.2)	3/16 (4.8)	1/32 (0.8)	10	
A-06424-67	1/8 (3.2)	1/4 (6.4)	1/16 (1.6)	21	
A-06424-65	5/32 (4.0)	7/32 (5.6)	1/32 (0.8)	10	
A-06424-66	3/16 (4.8)	1/4 (6.4)	1/32 (0.8)	9	
A-06424-03	3/16 (4.8)	5/16 (8.0)	1/16 (1.6)	13	
A-06424-69	3/16 (4.8)	7/16 (11.2)	1/8 (3.2)	22	
A-06424-71	1/4 (6.4)	3/8 (9.6)	1/16 (1.6)	12	
A-06424-72	1/4 (6.4)	7/16 (11.2)	3/32 (2.4)	17	
A-06424-74	1/4 (6.4)	1/2 (12.8)	1/8 (3.2)	17	
A-06424-75	5/16 (8.0)	7/16 (11.2)	1/16 (1.6)	10	
A-06424-76	5/16 (8.0)	1/2 (12.8)	3/32 (2.4)	16	
A-06424-12	3/8 (9.6)	1/2 (12.8)	1/16 (1.6)	10	
A-06424-79	3/8 (9.6)	5/8 (16.0)	1/8 (3.2)	14	
A-06424-19	1/2 (12.8)	11/16 (17.6)	3/32 (2.4)	10	
A-06424-81	1/2 (12.8)	3/4 (19.1)	1/8 (3.2)	10	

VICI® Valco Instruments Co. Inc.
VICI AG International

Valco Valves

TOP▲

1/16" fittings, 0.75 mm ports (.030")

Multiposition valves - SD configuration - low pressure - MW Type

1/16" fittings, 0.75 mm ports (.030")
200°C max, 400 psi gas
N60 stainless valve body, Valcon E rotor

Product numbers

Select to jump to product numbers.

4 position 10 position
6 position 12 position
8 position 16 position

Further reference

Which valve do I need?
Valve actuation
About standoff assemblies

Properties of metals
Properties of rotor materials

PRODUCTS

What's new
Actuators
Calibration gas standards
Columns
Fittings
Flow, pressure, and on/off controllers
Gas purifiers
GC accessories
GC detectors
HayeSep porous polymers
Injectors/valves
Liquid handling
Portable gas monitors
Syringes
Tools
Trace gas analyzers
Tubing

CUSTOMER SERVICE

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Catalog request
Ordering information
Returns/repairs
Contact us

VICI

About us
Photo tour
Upcoming trade shows

8 position valves - *1/16" fittings, 0.75 mm ports (.030") - SD configuration - low pressure*

Includes stainless steel nuts and ferrules.
Standard electric actuator:
110 VAC for USA; 110/230 VAC to 24 VDC power supply for international.
Microelectric actuator: 24 VDC, with 110/230 VAC to 24 VDC power supply.

Actuation	Standoff	Product No.
Manual (not recommended)	2"	2CSD8MWE
	3"	3CSD8MWE
	4"	4CSD8MWE
	6"	6CSD8MWE
With air actuator	none	ACSD8MWE
	2"	A2CSD8MWE
	3"	A3CSD8MWE
	4"	A4CSD8MWE
	6"	A6CSD8MWE
With standard electric actuator	none	ECSD8MWE
	2"	E2CSD8MWE
	3"	E3CSD8MWE
	4"	E4CSD8MWE
	6"	E6CSD8MWE
With microelectric actuator	none	EMTCSD8MWE
	2"	EMT2CSD8MWE
	3"	EMT3CSD8MWE
	4"	EMT4CSD8MWE
	6"	EMT6CSD8MWE

TOP▲
TOP▲

Replacement parts	Product No.
Valve *(for use with existing actuator)*	DCSD8MWE
Rotor	SSACSD8MWE

Appendix III

The following pages show the technical information regarding SF_6 gas its by-products and handling procedures:

BOC

Sulphurhexaflouride SF_6 gas data and safety sheet

US Environmental Protection Agency

By-products of Sulphurhexaflouride use in the electric power Industry

The University of Liverpool

SF_6 gas Handling Procedure

CK Gas Products

Certificates of Composition for concentrations of SF_6 in air (200 ppm, 50ppm and 20ppm)

BOC Special Gases

Gas data and safety sheet

Sulphur hexafluoride SF_6

This product is available in a variety of grades and container sizes. Please contact our Sales Office for specific details on our current range.

Container contents should not be identified by colour alone. Containers are stencilled/labelled sulphur hexafluoride. In the case of mixtures containing sulphur hexafluoride the containers are stencilled with the names of all the mixture components together with their respective concentrations.

In some instances, container valves are protected from mechanical damage by a detachable dome cover or guard. Where provided, this device must be correctly fitted when the container is not in use and when returning it to BOC.

It is important to use the correct pressure/flow control equipment. The choice of suitable equipment is dependent on the gas purity and the user's operating requirements. Contact BOC Special Gases Sales Office for advice.

Physical Properties (Pure)

Molecular weight	146·
Vapour pressure (20°C)	21·08 bar
Specific volume (20°C, 1 atm)	165 m
Sublimation point (1 atm)	−63·8
Density, gas (20°C, 1 atm)	6·07
Density, liquid (−50·8°C)	1·88 g/
Critical temperature	45·55
Dielectric constant, gas (20°C, 1 atm)	1·00
Specific gravity, gas (air=1)	5·
Colourless	
Odourless	

SUBSTANCE IDENTIFICATION (UN) NO.	10
HAZARD IDENTIFICATION NO.	
EMERGENCY ACTION (HAZCHEM) CODE	2I

Safety

WARNING: ASPHYXIANT GAS

Hazardous properties
Toxicity:
Exposure limit (TLV) 1000ppm (8hr TWA)
1250ppm (10 min TWA)
Asphyxiant at high concentrations.
Vapour much heavier than air.
Liquid in container under vapour pressure of about 21 bar(g).
Thermal or electrical decomposition of sulphur hexafluoride may produce toxic substances.
Liquid on skin may produce cold burns.

Safety precautions (see reverse side)
Containers in use should be in open air or in a well ventilated area.
Protect from sources of heat.

Material compatibility
As sulphur hexafluoride is non-corrosive common metals are acceptable.
Copper, stainless steel and aluminium are resistant to the decomposition products at 150°C.
All equipment must be able to withstand the process pressures.

Leak detection
Apply leak detection solution to suspect sites on lines and equipment. Bubbling shows up leaks. Electronic leak detection equipment may be used.

Toxicity and Symptoms
Sulphur hexafluoride is not considered to be toxic, but will not support life and at high concentrations acts as an asphyxiant by displacement of oxygen. Symptoms of asphyxiation may include rapid and gasping respiration, rapid fatigue, nausea, vomiting, cyanosis and may lead to loss of consciousness and death from anoxia.

Emergency Action

Inhalation (asphyxiation conditions)
Minimising personal risk, immediately rem victim to uncontaminated area. Ensure the no obstruction to the airway. If breathing v or stopped apply artificial ventilation with ultaneous administration of oxygen, prefer using oxygen resuscitator. Summon ambula Keep warm and rested.

Skin contact (cold burns)
Irrigate affected area with tepid water for at 15 minutes. Apply sterile dry dressing and as for a thermal burn. Seek medical advice as as possible.

Leaking container
If container in enclosed area evacuate the Minimising risk of asphyxiation, check conta valve closed. Move container to fume roor open space downwind and away from pers

Action in event of fire
In general, vacate area, call fire brigade. If ur to extinguish fire, keep surrounding conta cool with water hosed from a safe distance. In fire brigade of potential danger of exploding rocketing containers.

Note: Products of thermal decomposition are t

Emergency 24hr service 01-542 6677

BOC

Safety Data Sheet

Product : Sulphur hexafluoride

MSDS Nr :300-00-0027BOC Version : 1 Date : 26 / 08 /

1 IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY

Product name Sulphur hexafluoride
Chemical formula SF6
Company identification see heading and/or footer
Emergency phone numbers see heading and/or footer

2 COMPOSITION/INFORMATION ON INGREDIENTS

Substance/Preparation Substance.
Components/Impurities Contains no other components or impurities which will influence the classification of the product.
CAS Nr 02551-62-4
EEC Nr (from EINECS) 2198542

3 HAZARDS IDENTIFICATION

Hazards identification Liquefied gas
In high concentrations may cause asphyxiation.

4 FIRST AID MEASURES

Inhalation In high concentrations may cause asphyxiation. Symptoms may include loss of mobility/consciousness. Victim may not be aware of asphyxiation.
Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if breathing stopped.
Skin/eye contact Immediately flush eyes thoroughly with water for at least 15 minutes.
In case of frostbite spray with water for at least 15 minutes. Apply a sterile dressing.
Obtain medical assistance
Ingestion Ingestion is not considered a potential route of exposure.

5 FIRE FIGHTING MEASURES

Specific hazards Exposure to fire may cause containers to rupture/explode.
Non flammable
Hazardous combustion products If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition:
hydrogen fluoride
sulphur dioxide
Suitable extinguishing media All known extinguishants can be used.
Specific methods If possible, stop flow of product.
Move container away or cool with water from a protected position.
Special protective equipment for fire fighters Use self-contained breathing apparatus and chemically protective clothing.

6 ACCIDENTAL RELEASE MEASURES

Personal precautions Evacuate area.
Wear self-contained breathing apparatus when entering area unless atmosphere is proved to be safe.
Ensure adequate air ventilation.
Environmental precautions Try to stop release.
Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous.
Clean up methods Ventilate area.

7 HANDLING AND STORAGE

Handling and storage Suck back of water into the container must be prevented.
Do not allow backfeed into the container.

- valve protection device (where provided) is correctly fitted
- adequate ventilation.
- compliance with applicable regulations.

15 REGULATORY INFORMATION

Number in Annex I of Dir 67/548 Not included in Annex I.
EC Classification Proposed by the industry
Not classified as dangerous substance..
Labelling of cylinders
Symbols Road transport symbols are used and selected according to the most stringent product classification - EC or ADR .
Label 2: non flammable non toxic gas
-Risk phrases RAs Asphyxiant in high concentrations.
-Safety phrases S9 Keep container in well ventilated place.
S23 Do not breathe the gas.

16 OTHER INFORMATION

Ensure all national/local regulations are observed.
The hazard of asphyxiation is often overlooked and must be stressed during operator training.
Contact with liquid may cause cold burns/frost bite.
Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.
Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

End of document.
Number of pages : 3

Byproducts of Sulfur Hexafluoride (SF_6) Use in the Electric Power Industry

Prepared for

U.S. Environmental Protection Agency
Office of Air and Radiation
Global Programs Division
1200 Pennsylvania Avenue, NW
Washington, DC 20460

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January 2002

Forward

This document provides summary information on sulfur hexafluoride (SF_6) byproducts. It was prepared for the U.S. Environmental Protection Agency (U.S. EPA), Global Programs Division by ICF Consulting, Inc., under Contract No. 68-W5-0068, Work Assignment No. 0005AA-83. This document was developed as a service to partners of the *SF_6 Emissions Reduction Partnership for Electric Power Systems*. The information presented in this document does not replace existing regulations or guidance regarding these compounds. Rather, this document was designed solely as an overview of the most significant byproducts identified to date. If you have suggestions and/or information that would improve this document, please send them to

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or send an electronic mail to Blackman.Jerome@epa.gov. For more information on the *SF_6 Emissions Reduction Partnership for Electric Power Systems*, see http://www.epa.gov/highgwp1/sf6/index.html.

Contents

1. Introduction and Background

Sulfur hexafluoride (SF_6) is a relatively nontoxic gas used in a number of applications for its inert qualities. The dielectric and other physical and chemical properties related to its lack of reactivity have led to the extensive use of SF_6 as an insulating medium in switching equipment (e.g., circuit breakers) by electric utilities. While SF_6 is inert during normal use, when electrical discharges occur within SF_6-filled equipment, toxic byproducts can be produced that pose a threat to health of workers who come into contact with them. This paper discusses these byproducts and how they are formed, and also summarizes relevant health and safety concerns, as well as handling, detection, and safety procedures and guidelines.

U.S. EPA produced this background paper as a service to its partners in the *SF_6 Emission Reduction Partnership for Electric Power Systems*. This is a voluntary program in which partner companies agree to reduce SF_6 emissions through technically and economically feasible actions. SF_6 is a potent and persistent greenhouse gas, with a global warming potential approximately 24,000 times greater than carbon dioxide over a 100-year time horizon and a residency in the atmosphere of more than 3,000 years. Although SF_6 is critical to the reliable distribution of electricity, program participants recognize the importance of careful management and responsible use.

2. Formation and Concentrations of SF_6 Byproducts

Formation of SF_6 Byproducts

SF_6 can decompose into byproducts when exposed to four types of electric discharges (CIGRE[1] 1997):

- partial corona discharges caused by insulation defects;
- spark discharges that occur at insulation defects or during switching operations;
- switching arcs that occur in load break switches and power circuit breakers; and
- failure arcs that occur due to insulation breakdown or switchgear interruption failure.

Each discharge can result in different mixtures and concentrations of byproducts.

Concentrations of SF_6 Byproducts

Numerous studies have characterized the byproducts of SF_6. Dervos and Vassiliou (2000) have summarized the most important ones (considering toxicity and risk) and the amounts of each formed under conditions similar to those found in gas insulated switchgear (GIS) equipment (see Table 1). These data were obtained by exposing SF_6 to repeated sparking under experimental conditions, and thus the decomposition products and concentrations formed under actual conditions can vary depending on the equipment used and the type of electrical discharge (CIGRE 1997).

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[1] CIGRE (the International Council on Large Electric Systems) is a permanent non-governmental and non-profit-making international association based in France. This group has established a working group (Study Committee 23) that is focused on concerns related to substations, including SF_6 and its byproducts. The web site established by Study Committee 23 is located at http://www.cigre-sc23.org.

Table 1. Gaseous SF_6 Decomposition Byproducts and Typical Concentrations During Repeated Sparking

Chemical Formula	Chemical Name	Chemical Abstracts Service Registry Number	Experimental Concentration (percent by volume)[a]
HF	Hydrogen fluoride	7664-39-3	1.0
SOF_2 (SF_4)[b]	Thionyl sulfide (sulfur tetrafluoride)	7783-42-8 (7783-60-0)	0.5
SOF_4	Sulfur tetrafluoride oxide	13709-54-1	0.085
SiF_4	Silicon tetrafluoride	7783-61-1	0.085
S_2F_{10} (SF_5)[c]	Disulfur decafluoride	5714-22-7	0.025
SO_2F_2	Sulfuryl fluoride	2699-79-8	0.006
SO_2	Sulfur dioxide	7446-09-5	0.002

Table adapted from Dervos and Vassilion (2000).

[a] Note that these concentrations represent the measured concentration for the experimental conditions studied. The conditions were designed to simulate a real sparking occurrence; however, actual air concentrations in the vicinity of GIS will vary from these data.

[b] SF_4 is readily hydrolyzed to SOF_2.

[c] S_2F_{10} is referred to by some authors as sulfur pentafluoride or SF_5.

Additional byproducts that may be formed through arcing or other electrical discharges include SF_2, SOF_{10}, $S_2O_2F_{10}$, and H_2S, as well as a number of metal fluorides (e.g., copper fluoride (CuF_2), aluminum fluoride (AlF_3)) and tungsten compounds (e.g., WF_6, WO_3) (CIGRE 1997; U.S. EPA 2001a).

3. Health and Safety Concerns

Information on SF_6 byproducts has improved substantially in recent years. In its 1991 report, CIGRE identified only three gaseous SF_6 byproducts that pose a significant health threat (taking into account reaction quantities and toxicity): SOF_2, SO_2, and HF (Mauthe and Pettersson 1991). More recent research has identified S_2F_{10} as the byproduct of greatest concern due to its relatively high toxicity (James et al. 1993; Dervos and Vassiliou 2000), and occupational safety organizations have examined occupational exposures for several additional gaseous SF_6 byproducts.

Human Health Effects

According to information listed in the Hazardous Substances Databank (HSDB), gaseous SF_6 byproducts such as SF_4, SiF_4, SO_2F_2, SO_2, and HF are extremely irritating to the eyes, nose, and throat (NLM 2001). Other human health effects of these gases include pulmonary edema, skin and eye burns, nasal congestion, and bronchitis due to their corrosive characteristics. Solid byproducts such as AlF_3 and CuF_2 dusts are also irritating to exposed skin and eyes, and the nose, throat, and lungs when inhaled (NLM 2001). If copper salts are inhaled in sufficient concentration so that it reaches the gastrointestinal tract (via cough and mucociliary mechanisms), they act as irritants producing salivation, nausea, vomiting, gastric pain, hemorrhagic gastritis, and diarrhea (NLM 2001).

Several incidents involving human exposure to possible SF_6 byproducts have been reported.

- In the U.S., six workers were exposed during repair work on electrical equipment (Kraut and Lilis 1990). The workers experienced symptoms including burning/watering eyes, nasal irritation/epistaxis, throat irritation, chest tightness/wheezing/shortness of breath, coughing (in one case producing blood), nausea/vomiting, fatigue, and headaches. Most symptoms occurred immediately following or up to one week after the exposure event. Some workers' symptoms did not resolve until a month later or (in one case) a year later. No long-term physical effects were observed. Chemical evaluation at the site qualitatively identified the presence of SF_4.

- In the U.K., two workers collapsed after entering an SF_6 storage tower (James et al. 1993). One of the workers suffered pulmonary edema for the three days following exposure. No long term effects were reported for either worker. Following the incident, both SF_6 and SO_2F_2 were detected at levels that exceeded occupational exposure limits.

- In the Netherlands in 1989, an accident was reported involving two people who were exposed to unidentified substances resulting from a switchgear equipment failure (Mauthe and Pettersson 1991). The equipment contained SF_6; upon failure, a small amount of powder was observed (likely solid metal fluorides). Both people recovered within two weeks.

- A case of serious injury was reported to CIGRE in which an electrician repairing a circuit breaker was exposed to SF_6 decomposition products released by the equipment (Mauthe and Pettersson 1991). The worker lost consciousness and then awakened with a burning sensation in his chest. The worker's lung capacity was reduced by 45 percent. (CIGRE reports that had oxygen been administered more quickly, the damage would have been greatly reduced.)

- Several instances of minor skin irritation from exposure to SF_6 decomposition products have been reported to CIGRE (Mauthe and Pettersson 1991).

These instances of human exposure provide useful anecdotal evidence of the possible human health effects due to exposure to SF_6 byproducts, although specific byproduct compounds were not identified in all cases.

Cell and Animal Toxicity Data

Cell culture toxicity tests have been performed on S_2F_{10} and other SF_6 byproducts (summarized in James et al. 1993). The tests results indicate that S_2F_{10} is more than 43 times more toxic to cell cultures than the other SF_6 byproducts tested (SOF_2, SF_4, SOF_4, SiF_4, SO_2F_2, SO_2, HF). Additionally, whole animal toxicity studies have further characterized the toxicity of S_2F_{10} and other SF_6 byproducts. A complete summary of these data is beyond the scope of this paper, but specific animal toxicity information for SF_4, SiF_4, SO_2F_2, SO_2, HF, AlF_3 can be found in HSDB (NLM 2001). Animal studies indicate that these byproducts are extremely irritating when inhaled. Animals exposed to these gases via inhalation exhibit lung damage (e.g., lung irritation, edema, and hemorrhages) (Dervos and Vassiliou 2000; HSDB 2001).

5. Handling, Detection, and Safety Procedures and Guidelines

Numerous guidelines have been published regarding the handling, detection, and safety of SF_6 gas and its byproducts. These guidelines basically specify that employees minimize exposure to SF_6 byproducts by wearing protective equipment when handling and disposing SF_6 byproducts and by meeting specific exposure concentration standards.

Handling Procedures and Guidelines

SF_6 recycling and handling guidelines are described in detail in CIGRE guide number 117 (CIGRE 1997). Procedures specific to individual manufacturers' equipment types are also reported to be available directly from manufacturers. SF_6 handling procedures as provided by utility partners can be found on U.S. EPA's *SF_6 Emissions Reduction Partnership for Electric Power Systems* web page http://www.epa.gov/highgwp1/sf6/ (U.S. EPA 2001a). These guidelines often include procedures for handling hazardous SF_6 byproducts. U.S. EPA has also prepared a catalog that lists guidelines and standards for the handling and management of SF_6 (U.S. EPA 2001b).

Detection Procedures and Guidelines

SF_6 byproducts are difficult to detect chemically under normal working conditions. The presence of various SF_6 electrical discharge decomposition products and impurities (as well as the presence of SF_6 itself) makes measurement of the different byproducts problematic. A recent report in *Transmission and Distribution World* summarized methods that may allow for on-site and field monitoring of SF_6 byproducts with portable instrumentation (Baumbach et al. 2000). The *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997) presents measurement methods and signs and symptoms of exposure for S_2F_{10}, SF_4, SO_2, HF, and SO_2F_2, as well as SF_6.

SF_6 byproducts such as SOF_3 and SF_4 have a strong irritating "rotten egg" odor at low concentrations, and, at high concentrations, are irritating to the eyes, nose, throat, and lungs (U.S. EPA 2001; NLM 2001). Solid byproducts (i.e., metal fluoride byproducts) are white, gray, or tan powders that often can be observed when present and are irritating to exposed skin (Edison Technical Center 1997; U.S. EPA 2001a; NLM 2001). However, these gross physical indicators of the presence of byproducts should not be relied upon as safety mechanisms due to the possibility of severe injury, especially given that the most toxic byproduct, S_2F_{10}, is generally odorless in pure form at typical environmental temperature.

Safety Procedures and Guidelines

Safety precautions for hazardous SF_6 byproducts are often addressed in SF_6 handling procedures for gas-insulated electrical equipment. (See the electric utility partners' SF_6 handling procedures on U.S. EPA's web page http://www.epa.gov/highgwp1/sf6/ (U.S. EPA 2001a). Also see the U.S. EPA catalog – available from the same web page – of SF_6 guidelines and standards (U.S. EPA 2001b).) Many SF_6 handling procedures require the worker to wear protective clothing and an approved respirator when the presence of decomposition products are suspected (e.g., when the SF_6-filled breakers are exposed to a severe arc for an abnormal period of time due to improper operation of the breaker). Industrial hygiene practices can be found in the *NIOSH Pocket Guide to Chemical Hazards* (NIOSH 1997), including respirator selections, exposure limits, signs and symptoms of exposure, and procedures for emergency treatment for S_2F_{10}, SF_4, SO_2, HF, SO_2F_2, fluorides, as well as SF_6.

Table 2 compiles the available occupational safety standards for the gaseous byproducts identified in Table 1 of this paper. SF_6 is included for reference. Table 3 lists exposure limits for fluorides, aluminum, and copper compound dusts. The parameters presented in Tables 2 and 3 are defined below.

- Permissible exposure limit - ceiling (PEL-ceiling): Defined by the Occupational Safety and Health Administration (OSHA), the PEL-ceiling is a specified concentration of the chemical in air that must not be exceeded during any part of the working exposure for any amount of time.

- Recommended exposure limit - ceiling (REL-ceiling): The REL - ceiling is concentration of the chemical in air that should not be exceeded, as recommended by the National Institute for Occupational Safety and Health (NIOSH).

- Recommended exposure limit - time-weighted average (REL-TWA): The REL-TWA is the time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek that should not be exceeded, as recommended by NIOSH.

- Permissible exposure limit - time-weighted average (PEL-TWA): Defined by OSHA, the PEL-TWA is the time-weighted average concentration that must not be exceeded during any 8-hour work shift of a 40-hour work-week.

- Short-term exposure limit (STEL): Defined by OSHA, the STEL is the concentration that must not be exceeded over a 15-minute period.

- Recommended short-term exposure limit (RSTEL): The RSTEL is a 15-minute time-weighted average concentration that should not be exceeded at any time during a workday, as recommended by NIOSH.

- Level immediately dangerous to life or health (IDLH): Developed by NIOSH, the IDLH is the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without irreversible health effects (designed to aid in the selection of a respirator only).

- Threshold limit value - ceiling (TLV-C): Established by the American Conference of Governmental Industrial Hygienists (ACGIH), the TLV-C is a specified concentration of the chemical in air that should not be exceeded during any part of the working exposure for any amount of time.

- Threshold limit value - time-weighted average (TLV-TWA): Established by ACGIH, the TLV-TWA is a the time-weighted average concentration that should not be exceeded based on a normal 8 hour work day/40 hour work week.

Occupational exposure limits were not located for some of the SF_6 byproducts (including SOF_4 and SiF_4). The occupational standards listed in Tables 2 and 3 were developed by occupational health organizations in the United States. CIGRE literature and information in HSDB indicate that international exposure values also exist for some SF_6 byproducts (Mauthe and Pettersson 1991; NLM 2001).

Table 2. Available Inhalation Exposure Limits for SF_6 and Gaseous Byproducts of SF_6

Substance	Parameter	Exposure limit value	Defining organization
S_2F_{10} (SF_5) (sulfur decafluoride or pentafluoride)	PEL-TWA	0.025 ppm	OSHA
	PEL-ceiling [a]	0.01 ppm	OSHA
	REL-ceiling	0.01 ppm	NIOSH
	IDLH	1 ppm	NIOSH
	TLV-C	0.01 ppm	ACGIH
SF_4 (sulfur tetrafluoride)	PEL-ceiling [b]	0.1 ppm	OSHA
	REL-ceiling [c]	0.1 ppm	NIOSH
	TLV-C	0.1 ppm	ACGIH
SO_2 (sulfur dioxide)	PEL-TWA [b]	2 ppm	OSHA
	STEL [b]	5 ppm	OSHA
	REL-TWA	2 ppm	NIOSH
	RSTEL	5 ppm	NIOSH
	IDLH	100 ppm	NIOSH
	TLV-TWA	2 ppm	ACGIH
HF (hydrogen fluoride)	PEL-TWA	3 ppm	OSHA
	STEL [b]	6 ppm	OSHA
	REL-ceiling	6 ppm	NIOSH
	REL-TWA	3 ppm	NIOSH
	IDLH	30 ppm	NIOSH
SO_2F_2 (sulfuryl fluoride)	PEL-TWA	5 ppm	OSHA
	STEL [b]	10 ppm	OSHA
	REL-TWA	5 ppm	NIOSH
	RSTEL	10 ppm	NIOSH
	IDLH	200 ppm	NIOSH
SF_6 (sulfur hexafluoride)	PEL-TWA	1,000 ppm	OSHA
	REL-TWA [c]	1,000 ppm	NIOSH
	TLV-TWA	1,000 ppm	ACGIH

All values listed in this table were cited in ACGIH (1989), James et al. (1993), NIOSH (1997), or OSHA (2000).
ppm = parts per million; ppb = parts per billion; ppm and ppb are given by volume in air.

[a] The PEL-TWA of 0.025 ppm was revised in 1989 to a PEL-ceiling value of 0.01 ppm; however, enforcement of the new limit of 0.01 ppm has been stayed by OSHA, until it publishes a notice in the Federal Register regarding an available sampling and analytical technique.

[b] PEL or STEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the "general duty clause" in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs and STELs.

[c] NIOSH has not established an IDLH value for this substance.

Table 3. Available Inhalation Exposure Limits for Solid Byproducts of SF_6

Substance	Parameter	Exposure limit value	Defining organization
Fluorides (measured as fluorine (F))	PEL-TWA	2.5 mg/m^3	OSHA
	TLV- TWA	2.5 mg/m^3	ACGIH
Aluminum soluble salts (measured as aluminum (Al))	PEL-TWA[a]	2 mg/m^3	OSHA
	REL-TWA	2 mg/m^3	NIOSH
Copper dusts (e.g., CuF_2)	PEL-TWA	1 mg/m^3	OSHA
	REL-TWA	1 mg/m^3	NIOSH
	IDLH	100 mg/m^3	NIOSH
	TLV-TWA	1 mg/m^3	ACGIH

All values listed in this table were cited in NLM (2001) and NIOSH (1997)

[a] PEL was vacated by the U.S. Circuit Court of Appeals on June 30, 1993; however, OSHA may enforce it under the "general duty clause" in Section 5(a)(1) of the Occupational Safety and Health Act. Some states enforce vacated PELs.

The Department of Transportation (DOT) provides guidance for emergency response for transportation incidents involving hazardous materials in its *2000 Emergency Response Guidebook.* Health warnings, fire mitigation, evacuation procedures, protective clothing prescriptions, and first aid procedures are available for SO_2F_2 (DOT no. 2191) in Guide 123 and SF_4 (DOT no. 2418) and HF (DOT no. 1052) in Guide 125 (DOT 2000).

5. References

American Conference of Government Industrial Hygienists (ACGIH). 1989. *Threshold Limit Values and Biological Exposure Indices for 1989-1990.* Cincinnati, Ohio.

Baumbach, J.I., Pilzecker, P., Trindade, E., and J. Meinders. 2000. Diagnosing the health of SF_6 switchgear. *Transmission and Distribution World* Vol. 52 (1), Jan 1, 2000, 3 pp.

International Council on Large Electric Systems (CIGRE). 1997. *SF_6 Recycling Guide.* Publication number 117; Task Force 23.10.01. August 1997.

Department of Transportation (DOT). 2000. 2000 Emergency Response Guidebook. A Guidebook for First Responders During the Initial Phase of a Dangerous Materials Incident. Internet site at http://hazmat.dot.gov/gydebook.htm.

Dervos, C.T., and P. Vassiliou. 2000. Sulfur hexafluoride (SF_6): Global environmental effects and toxic byproduct formation. *J. Air and Waste Manage. Assoc.* 50:137-141.

Edison Technical Center. 1997. *Insulating Materials for Distribution Switchgear in Today's Environment.* Internet site located at http://169.207.59.145/Library/TheLine/pdf/97-04/04-97-etc-01.html. Site dated April 1997; accessed September 2000.

Greenberg, L.A., and D. Lester. 1950. The toxicity of sulfur pentafluoride. *Arch. Indust. Hygiene and Occupat. Med.* 2:350-353. [cited in James et al. 1993]

James, D.R., I. Sauers, G.D. Griffin, R.J Van Brunt, J.K. Olthoff, K.L. Stricklett, F.Y. Chu, J.R. Robins, and H.D. Morrison. 1993. Investigation of S_2F_{10} production and mitigation in compressed SF_6-insulated power systems. *IEEE Electrical Insulation Magazine* 9(3):29-51.

Kraut, A. and R. Lilis. 1990. Pulmonary effects of acute exposure to degradation products of sulphur hexafluoride during electrical cable repair work. *British Journal of Industrial Medicine* 47:829-832.

Mauthe,G., and K. Pettersson. 1991. Handling of SF_6 and its decomposition products in gas insulated switchgear (GIS). *Electra*, no. 136:69-89 (Part 1) and no 137:81-105 (Part 2). June 1991. (Publication of Working Group 23, International Council on Large Electric Systems (CIGRE)).

National Institute for Occupational Safety and Health (NIOSH). 1997. *NIOSH Pocket Guide to Chemical Hazards.* U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, Washington, D.C. NIOSH Publication no. 97-140; NTIS no. PB-97-177604. Internet site located at http://www.cdc.gov/niosh/npg/pgdstart.html.

National Library of Medicine (NLM). 2001. *Hazardous Substances Databank (HSDB).* Internet site located at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Occupational Safety and Health Administration (OSHA). 2000. Chemical Sampling Information. January 19. http://www.osha-slc.gov/dts/chemicalsampling/toc/toc_chemsamp.html

Renshaw, B., and M. Gates. 1946. "Di-sulfur decafluoride," in *Chemical Warfare Agents and Related Chemical Problems Parts I-II*, Office of Scientific Research and Development, National Defense Research Committee, Washington, D.C. NTIS no. PB-158508, Chapter 4, pp. 24-29. [cited in James et al. 1993]

Sauers, I., G.D. Griffen, D.R. James, R.J. Van Brunt, J.K. Olthoff, K.L. Stricklett, H.D. Morrison, M. Frechette, et al. 1995. *Investigation of S_2F_{10} production and mitigation in compressed SF_6-insulated power systems*. Final report. Volume 1: Executive Summary. Prepared under Cooperative Research and Development Agreement No. ORNL 90-0002. October 1995. ORNL/M-4314.

Sauers, I. 1998. Plasma Chem. *Plasma Process.* 8: 247-262. [cited in Sauers et al. 1995]

U.S. Environmental Protection Agency (U.S. EPA). 2001a. *SF_6 Emissions Reduction Partnership for Electric Power Systems: SF_6 Handling Procedures.* Internet web site at http://www.epa.gov/highgwp1/sf6/partner_resources/index.html

U.S. Environmental Protection Agency (U.S. EPA). 2001b. Catalog of Guidelines and Standards for the Handling and Management of Sulfur Hexafluoride (SF_6). Prepared for the U.S. EPA, Office of Air and Radiation, Global Programs Division. Prepared by ICF Consulting, Fairfax, VA, under Contract No. 68-W5-0068. July. http://www.epa.gov/highwp1/sf6/pdf/sf6utility7.pdf.

Van Brunt, R.J., and J.T. Herron. 1990. *IEEE Trans. Electr. Insul.* E1-25: 75-94. [cited in Sauers et al. 1995]

SF6 Gas Handling Procedure

1. Introduction

This module lists procedures required to safely perform installation, inspection, and maintenance work on sulfur hexafluoride (SF6) gas-insulated apparatus.

In common with numerous other chemicals used everyday in industry, SF6 gas and its decomposition products present no injury or illness problems it dealt with properly. As with other chemicals, health hazards may exist under particular conditions, if exposure or handling is careless or improper. All personnel designated to perform inspection or maintenance work on ABB SF6-insulated apparatus should read this module and follow all of the instructions herein.

1.1 Properties of SF6 Gas

In its pure, natural state, SF6 gas is colorless, odorless, and tasteless and possesses a low order of toxicity. The only danger in breathing pure SF6 gas is that it displaces oxygen and can cause suffocation. SF6 gas is chemically inert and non-flammable. The gas has a high dielectric strength and thermal properties conducive for insulating high voltage and quenching electrical arcs.

Refer to the addendum (at the end of this module) from the manufacturer for specific chemical details.

If SF6 gas if subjected to an electric arc heat causes the gas to decompose into potentially toxic by-products. (This gas also decomposes when exposed to other high temperature conditions such as heater filaments, smoking, welding, etc.) Fluorides of sulfur are the most toxic decomposition products and are in gaseous form. A molecular sieve (desiccant bag) containing activated alumina is provided in each pole tank. This molecular sieve eliminates most of these gaseous decomposition products. The less toxic metal fluorides are in the form of white, tan or gray powder. The amount of decomposition of the gas is a function of the intensity and duration of the arc.

Some of the SF6 decomposition products form corrosive and conductive compounds when exposed to moisture. These compounds, which can be harmful to human beings, are also aggressive towards materials within the circuit breaker, especially insulating surfaces if subjected to prolonged exposure. That's why it's best not to perform breaker maintenance on rainy, humid days.

By weight SF6 gas is approximately five times heavier than air and tends to diffuse towards the pull of gravity and pools in low places. As a result of this pooling, the gas displaces oxygen and can cause suffocation without warning if the oxygen content of air is reduced from the normal 20 percent to less than 13 percent.

In the presence of moist air, noxious decomposition products have a characteristic odor of rotten eggs.

DANGER

Since SF6 gas displaces oxygen, avoid inhaling SF6 gas. Oxygen deficiency can cause nausea and drowsiness. Prolonged exposure to this gas in a confined space can cause serious breathing difficulty and suffocation.

Avoid skin or eye contact with the decomposition products because they can cause skin rashes, eye irritation, and chemical burns.

In the presence of moist air, noxious decomposition products have a characteristic odor of rotten eggs. Avoid inhaling these by-products because, unprotected prolonged exposure can injure the respiratory tract. Wear the prescribed protective gear indicated in sections 1.2.1 and 3.

1.2 Equipment Used to Handle SF6 Decomposition Products

The following equipment is used to perform maintenance on SF6 gas-insulated apparatus where decomposition products may be present:

- Hooded disposable coveralls – Tyvec, Durafab or equivalent-made of paper with nylon reinforcement material;
- Non-Disposable Neoprene Gloves – 14inch size;
- Non-Disposable Rubber Boots – 17 inch size over-the-shoe style;
- Clean, oil-free dry air supply with a capability to provide sufficient purging and ventilating capacity;
- Full-face Comfo II respirator or equivalent with twin cartridges for organic vapors and acid gases, i.e., GMC or equivalent;
- Supplied air-line respirator-MSA pressure demand type with Ultravue face piece and web bell-mounted demand respirator, 50 ft. of air supply hose, manifold with quick-disconnect and automatic shut-off outlets, cylinder pressure regulator, must have NIOSH/MESA approval No. TC-19C-93 or equivalent from other manufacturer;
- Respiratory compress air supply-300 lb. Approved portable tank with air meeting Grade D, ANSI Standard Z96.1-1974 with supply hose ideal pressure between 80 to 100 psig;
- Industrial wet or dry type vacuum cleaner with non-metallic attachments, micro staphicidal filter elements (particles to 0.3 microns) two 15-inch lengths of plastic hose and coupler;
- Cleaning solvent: denatured ethyl alcohol.

1.2.1 Protective Gear

Minimum required protective gear to be worn while handling SF6 gas-insulated apparatus are:

- Gloves;
- Full-face Comfo II respirator or equivalent with twin cartridges for organic vapors and acid gases, i.e., GMC or equivalent;

Full protective gear includes:

- Gloves;
- Hooded disposable coveralls;
- Non-Disposable Neoprene Gloves – 14 inch
- Non-Disposable Robber Boots – 17 inch, over-the-shoe style;
- Supplied air-line respirator.

2. SF6 Gas Handling Safety Practices

Safety practices when handling SF6-gas-insulated apparatus are:

- Perform SF6 gas handling, filling or reclaiming outdoors;
- If procedures involving SF6 gas insulated equipment must be done indoors, work in a well-ventilated room; make sure the ventilating equipment is operating;
- No smoking;
- No exposed heaters, flames, or arc-producing equipment should be used in the area while the gas is being handled;
- If-when handling used SF6 gas, the odor of rotten eggs is detected, personnel not wearing respiratory equipment should promptly evacuate the area;
- Correct any gas leaks at hose or filling connection at the breaker, on the service cart, or at the cylinder.

2.1 Storing SF6 Gas Cylinders

Pressurized cylinders, which contain SF6 gas, can be damaged or ruptured by careless handling.

Requirements for storing gas cylinders include:

- Store cylinders in a well-ventilated area;
- Secure the cylinders in a way to prevent them from falling or being knocked over.

2.1.1 Heating an SF6 Gas Cylinder

When filling during cold ambient temperatures, the cylinder may be heated any of the following methods to convert the liquid SF6 in the cylinder to a gaseous state:

- An electric blanket heater;
- Immersing the gas cylinder upright in a drum partially filled with warm water so that approximately half of the cylinder is immersed. Heat the water with a portable gas or electric heater.

WARNING

Never heat a gas cylinder with an open flame.

Energize heaters only when transferring the gas. When handling the cylinder, be sure that the temperature in the cylinder does not exceed 100°F (38°C).

3. Maintenance of SF6 Gas Insulated Apparatus

After an SF6 electrical apparatus has been in service, it should be assumed that hazardous decomposition might be present.

Before performing any maintenance on SF6 gas-insulated apparatus, review sections 1 and 2 of this module. Perform the initial inspection of the apparatus wearing at a minimum, gloves and a full-face respirator. If significant amounts of solid decomposition products or noxious gases are present when opening a pole unit, wear full protective gear (as listed in section 1.2.1) and proceed as per section 3.1.

If a tent-like enclosure is used around the apparatus, use a dry air ventilation system while performing maintenance work.

If no decomposition products are found:

1. Purge the apparatus thoroughly with dry air from a suitable source.

   Important: Do not purge with damp or set air as it can endanger the integrity of insulation materials and prolong dry-out and reconditioning time.

   It is only safe to assume that there may be hazardous gaseous products present. All personnel should stand clear of the apparatus during purging.

2. Allow purging to continue long enough to assure a minimum of at least 10 complete air changes through the total apparatus before working on the equipment. If the SF6 gas has not been fully evacuated from the apparatus prior to purging, perform a minimum of 100 air changes.

3. Reduce the purging air supply to a low level (approximately 10 air changes per hour) to provide continuous ventilation of the apparatus while personnel are working internally in the apparatus.

3.1 Removing SF6 Decomposition Products

If significant arc powders or noxious odors are detected upon opening a pole unit or any other apparatus:

1. Wear full protective clothing and a supplied air full-face respirator.

2. Establish a restricted safety zone around the equipment. Personnel cannot enter this zone without wearing full protective gear (defined in section 1.2.1). If performing this work outdoors, the zone may need to be extended downwind of the work site.

3. Use a vacuum cleaner equipped with filters as described in section 1.2; this vacuum cleaner should be used exclusively for removing SF6 decomposition products.

4. Wipe up any remaining powdered decomposition products with rags using denatured ethyl alcohol.

5. Remove and dispose the molecular sieve (desiccant) within the apparatus as per section 4; keep the full protective gear on.

6. Place materials used and retrieved in clean-up operations in large plastic or metal containers. These containers serve as refuse containers.

7. Proceed with purging as per section 3 after removing all decomposition products.

4. Disposing of Decomposition Products

Dispose of decomposition products outdoors since corrosive or toxic gases may evolve from the solid arc products or from the molecular sieve (desiccant). Disposal of the SF6 residue involves neutralizing the decomposition products.

Notice: Wear full protective gear as per section 1.2.1 during disposal.

To properly dispose of decomposition product residue:

1. Place materials used and retrieved in clean-up operations in large plastic or metal containers. These containers serve as refuse containers.

2. Empty the vacuum cleaner housing and the absorption filter material into the container.

3. Note or measure the volume of material in the containers.

4. In a separate container (plastic pail), measure a volume of water 1.5 times that of the above refuse material. Empty the water into the refuse container pouring the water quickly at first then slowly. The water mixing with the SF6 refuse will produce some heat and foam.

5. Measure a quantity of soda ash (sodium carbonate) or lime (calcium oxide) equal to at least one-quarter the volume of the refuse and add this neutralizing agent to the water-refuse material.

6. Add the cleaning rags, protective clothing (even though it is disposable), along with the filters from the vacuum cleaner and respirator to the neutralizing mixture in the refuse container.

7. Allow the refuse container to stand uncovered for 24 hours.

8. Afterwards test the pH of the refuse mixture.

   The mixture should be at least slightly alkaline (greater than 7). If the pH is between 7 and 10, the refuse is now rendered harmless and may be disposed of in a normal manner as per local ordinances.

   If the solution pH is less than 7, it is still acidic and harmful; add soda ash or lime to neutralize the refuse mixture to a pH greater than 7 but less than 10. Then dispose of the material as per local ordinances.

4.1 Removing SF6 Gas Residue from Tools and Equipment

To clean tools and equipment that have been exposed to SF6 decomposition products:

1. Prepare a mild (10%) lime or soda ash solution and use this as the neutralizing solution.

2. Wash any hand tools, non-disposable protective gear, and equipment employed in the clean-up operation.

3. Vacuum some of this neutralizing solution through the hose and into the vacuum cleaner to neutralize particles adhering to this equipment.

4. Rinse all washed tools and equipment thoroughly with water.

5. Wash the rubber boots and Neoprene gloves in water.

CK GAS PRODUCTS LTD.

3 MURREL GREEN
BUSINESS PARK
HOOK
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Certificate of Composition 12549- 3- 1

Order No	100003038	Cylinder No	46797
Customer	Stock	Cylinder Valve	BS3
Our Ref	12356	Cylinder Size	5AL

Component	Requested Value	Certified Valu
SULFUR HEXAFLUORIDE	200PPM	200.6PPM
AIR	BALANCE	BALANCE

Pressure 130 Bar Volume 975 Litres Valid Until May 2008

Please note all units are in MOL% and mixture accuracy +/-2% Relative Mixtures trace to standards calibrated at the National Physical Laboratory, Teddington, Middlesex, England

Certified by A.J. BOULTON UN NO 1956 Date 23/05/2005

CK GAS PRODUCTS LTD.

3 MURREL GREEN
BUSINESS PARK
HOOK
HAMPSHIRE RG27 7GR
TEL:01256 766633
FAX:01256 766630
E-MAIL:sales@ckgas.com

Certificate of Composition 12549- 2- 1

Order No	100003038	Cylinder No	33491
Customer	Stock	Cylinder Valve	BS3
Our Ref	12356	Cylinder Size	5AL

Component	Requested Value	Certified Value
SULFUR HEXAFLUORIDE	50PPM	50.5PPM
AIR	BALANCE	BALANCE

Pressure 130 Bar Volume 975 Litres Valid Until May 2008

Please note all units are in MOL% and mixture accuracy +/-2% Relative Mixtures traceal to standards calibrated at the National Physical Laboratory, Teddington, Middlesex, England

Certified by A.J. BOULTON UN NO 1956 Date 23/05/2005

CK GAS PRODUCTS LTD.

3 MURREL GREEN
BUSINESS PARK
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FAX:01256 766630
E-MAIL:sales@ckgas.com

Certificate of Composition 12549- 1- 1

Order No	100003038	Cylinder No	31437
Customer	Stock	Cylinder Valve	BS3
Our Ref	12356	Cylinder Size	5AL

Component	Requested Value	Certified Value
SULFUR HEXAFLUORIDE	20PPM	20.2PPM
AIR	BALANCE	BALANCE

Pressure 130 Bar Volume 975 Litres Valid Until May 2008

Please note all units are in MOL% and mixture accuracy +/-2% Relative Mixtures traceab to standards calibrated at tne National Physical Laboratory, Teddington, Middlesex, England

Certified by A.J. BOULTON UN NO 1956 Date 23/05/2005

Appendix IV

The following pages show the recipe used on the CIRRUS^{TM} Mass spectrometer in order that mass spectra can be obtained from a number of different measurement points when using the an 8-way VICI valve in conjunction with tubing.

```
'Recipe created by Martin Kidman
'Creation date/time: 24/10/2005 17:24:14
'Created to take samples from tri stimulus model tests measuring SF6
'
'*****************************************************************
'* You may use any of the global variables declared    *
'* below in the User Subroutines, which you are free to modify *
'*****************************************************************
'{{RWIZ01
Option Explicit

'Global Wizard-declared variables
'You may freely use these in the User_Subroutines

Public DataPath, DataFilename
Public UserEndRecipeFlag                'Set this to True to stop the recipe
Public UserEndTriggerFlag               'Set this to True to stop the trigger stage (if it exists)
Public UserHoldFlag                             'Set this to True to suspend data storage (if Hold is enabled)
Public bQuietMode : bQuietMode = True   'To suppress message boxes
Public ThisInstrumentName                       'Set this to change the instrument connection
Public ControlUnitUses, SensorIDs       'Set these values to change the connection configuration
ThisInstrumentName = "Runtime Instrument"
ControlUnitUses = Array(4)
SensorIDs = Array(1)
Private Microvision                             'Use this to get or set the Microvision properties (if it exists)
Private bMicrovisionHasRVC
Private bInTriggerStage : bInTriggerStage = False       'True if waiting to trigger
Private TriggerRecipeStartTime  'Wizard will set this for you (if the recipe is triggered)
Private MainRecipeStartTime             'Wizard will set this for you
'}}RWIZ01

'Declare and initialise your global variables here
 Dim Current_Valve_Position
 Dim Scan_Delay
 Dim Scan_Start_Time
 Dim Scan_Count

 Private Sub User_OnEntry
        'User inserts initialization code here
        'At this time there are neither connected instruments or measurements
        Scan_Delay=20*(1/(24*60*60))
        Scan_Start_Time=0
        Recipe.TimerInterval=1000
 End Sub

 Private Sub UserInstrument_ConnectFail (Reason)
 End Sub

 Private Sub User_PreTrigger
        'User inserts pre-trigger code here
        'This code only runs if a trigger stage is included in the recipe
        'The Instruments (if any) and the trigger measurement (if appropriate) have been set up
        If IsObject(microvision) Then microvision.Cirrus.ValvePosition=Current_Valve_Position
        EventLog.AddMessage "Valve " & Current_Valve_Position+1 & " Open",False,"Valve Position"
 End Sub

 Private Sub User_Trigger_EndOfScan
 End Sub

 Private Sub User_PostTrigger
 End Sub

 Private Sub User_PreRun
        'User inserts pre-run code here
        'The Instruments and the scan measurements have been set up
        Dim DataWin,DataStream
        Scan.FreeRun=False
        With Streams.Create()
                .Fields.Add "Valve Position", fieldNumber
                .Initialise "Valve State", bufferHistory, 100
        End With
        For Each DataWin In Windows
                If DataWin.Type = viewAnaBar Or DataWin.Type = viewTrend Then
                        For Each DataStream In Streams
```

```
                                        If StrComp(DataStream.Name, "Valve State", 1) = 0 Then
DataWin.AddAnnotationStream DataStream, 2
                                Next
                        End If
                Next
                Open_Valve Current_Valve_Position
End Sub

Private Sub User_WriteToActionChannels (UserMeasurement)
        'This code only runs if Wizard-defined User Variables or Action Channels are included in the recipe
        'All the instrument data readings have been completely acquired
        'Example:
        'With UserMeasurement
        '       .Data("Name of channel").Value = xxx
        '       .Data("Name of channel").Pressure = xxx
        'End With
End Sub

Private Sub User_EndOfScan
        'User inserts end of scan code here
        'Do not write to Action channels here
        'Include UserEndRecipeFlag = True if required
        Scan_Count=Scan_Count+1
        If Scan_Count>=2 Then
                If Current_Valve_Position=7 Then
                        Open_Valve 0
                Else
                        Open_Valve Current_Valve_Position+1
                End If
                Scan_Count=0
                Scan_Start_Time=Now+Scan_Delay
        Else
                Scan.Resume
        End If

End Sub

Private Sub User_PostRun
        'User inserts post-run code here
        'The Scan and its measurements still exist
End Sub

Private Sub User_EndOfRecipe
        'User inserts end of recipe code here
        'The Scan and its measurements no longer exist
End Sub

Private Sub User_InitializeNextRecipe (TheNextScript)
        'Specialist user code to initialize variables or call functions in a chained-to recipe, if one exists.
        'This code runs after the next recipe has been started but before this one closes.
        'It is likely that, at this time, the only valid data from this recipe will be global variables.
        'Variables or functions in the chained-to recipe must be declared as 'Public'.
        'For example use  TheNextScript.PublicVariable = ThisScriptVar + 1
End Sub

Private Sub UserTimer_OnTimer
        'If enabled, this event will fire at the TimerInterval (milliseconds)
        'Enable it with a statement in eg User_PreRun such as
                'If TimerInterval = 0 Then TimerInterval = 1000
        'Use the Timer carefully because some recipes require that
        'the Wizard sets TimerInterval for its own purposes.
        If Scan_Start_Time<>0 Then
                If Now>=Scan_Start_Time Then
                        Scan_Start_Time=0
                        Scan.Resume
                End If
        End If
End Sub

Private Sub UserInstrument_QuadrupoleChange (TheMicrovision, ChangedBits)
End Sub

Private Sub UserInstrument_RVCChange (TheMicrovision, ChangedBits)
End Sub
```

```
Private Sub UserInstrument_DigitalChange (TheMicrovision, ThePort, ChangedBits)
End Sub

Private Sub UserInstrument_AnalogInputReading (TheMicrovision, TheInput)
End Sub

Private Sub UserInstrument_LinkDown (TheMicrovision, Reason)
End Sub

Sub Open_Valve(Valve)
        Dim Relay
        If Valve>7 Then Valve=7
        If Valve<0 Then Valve=0
        If IsObject(microvision) Then microvision.Cirrus.ValvePosition=Valve
  Current_Valve_Position=Valve
  If IsObject(Streams("Valve State")) Then
                With Streams("Valve State")
                        .AddRecord
                        .Fields("Valve Position").Value = Current_Valve_Position+1
                        .CommitRecord
                End With
        End If
        EventLog.AddMessage "Valve " & Current_Valve_Position+1 & " Open",False,"Valve Position"
End Sub

'*******************************************************
'Do not modify the code that appears below in gray text *
'*******************************************************
'{{RWIZ02
'General Wizard functions and procedures
'01002
Private MaxMass
Private bDoneWrongIntervalMsg
Private bDelayIsOk, bTimeIsOk, bUserIsOk, bScanCountIsOk, bUserVarIsOk, bAnalogIsOk, bDigitalIsOk, bPartialIsOk,
bRVCIsOk
Private PrevRVCStatus(1), PrevRVCValveOpen(1), PrevRVCDigitalInput(1), LastRVCStreamUpdateTime
Private LastDigIOStreamUpdateTime(1)
Private AnalogInFields, AnalogInSlopes, AnalogInOffsets, AnalogInLogScales, AnalogInPressures
Private DigIOFields()
AnalogInFields = Array("AI1", "AI2", "AI3", "AI4")
AnalogInSlopes = Array(1, 1, 1, 1)
AnalogInOffsets = Array(0, 0, 0, 0)
AnalogInLogScales = Array(False, False, False, False)
AnalogInPressures = Array(False, False, False, False)

Public Sub Recipe_Main
        '100011
        '100020
        '100030
        '100040
        '100050
        '100060
        '100070
        '100090
        '100100
        If Not ValidateAppVersion Then Exit Sub

        User_OnEntry
        FindAndConnectInstrument Microvision
        If Not IsObject(Microvision) Then Exit Sub
        StartTrigger
End Sub

Private Sub StartTrigger
        '350010
        'add the measurements for trigger
        SetUpTriggerMeasurements
        'Run the user code
        User_PreTrigger
        TimerInterval = 500
        bDoneWrongIntervalMsg = False
        'initialise the progress timer
        TriggerRecipeStartTime = Now
        bInTriggerStage = True
End Sub
```

```
Private Sub StartMainScan
        Dim PortNum

        '350021
        If TurnFilamentsOn() = vbCancel Then EndRecipe False
        'add the measurements for main
        SetUpMainMeasurements
        User_PreRun
        '58002500
        Scan.HistorySize = 500
        Scan.EventPrefix = "Main_"
        If IsObject(Microvision) Then
                If bMicrovisionHasRVC Then UpdateRVCStream Microvision
                With Microvision
                        For PortNum = 0 To .Digitals.Count - 1
                                If .Digitals(PortNum).ConnectedMask Then UpdateDigitalStream Microvision,
.Digitals(PortNum)
                        Next
                End With
                If TimerInterval = 0 Then TimerInterval = 5000                  'we need it to update our streams
        End If
        MainRecipeStartTime = Now
        Scan.Start
End Sub

Public Sub Main_EndOfScan
        'main recipe scan stage
        'end of scan actions
        Wizard_EndOfScan
        User_EndOfScan
        If AtEndOfMain() Then EndRecipe True
End Sub

Public Sub EndRecipe (AndStopScan)
        'Controlled closedown
        If Scan.IsScanning And AndStopScan Then
                User_PostRun
                Scan.Stop
        End If
        User_EndOfRecipe
        Wizard_EndOfRecipe
        Abort
End Sub

Public Sub Recipe_Exit
        'called by Process if the user aborts the recipe early
        'Note: Does not call User_PostRun.  If you need this to happen create a flag
        'that is checked in User_EndOfRecipe, and call User_PostRun from User_EndOfRecipe
        User_EndOfRecipe
        Wizard_EndOfRecipe
End Sub

'050000
Private Sub FindAndConnectInstrument (ConnectTo)
        '*****************************************************
        '* The connection is to be determined at run-time  *
        '* Ask the user, if necessary                      *
        '*****************************************************

        '050110
        '05012512
        '050130
        '05021110300__00100__10000

        Dim bBadInstrument, SourceID, EGainID

        ConnectTo = Empty
        On Error Resume Next
        Set ConnectTo = QueryConnectByUse(-1, -1, -1)

        If Err.Number <> 0 Then
                'ConnectInstrument generated an error
                GenerateError 4, Err.Description
                ConnectTo = Null
```

```
		Exit Sub
	End If
	If ConnectTo Is Nothing Then
		'we cancelled
		GenerateError 5, ""
		ConnectTo = Null
		Exit Sub
	End If

	'16100221
	'800004
	'check the connection and that the instrument has required performance
	With ConnectTo
		MaxMass = .Info.MVInfo.MaxMass
		If MaxMass < 150 Then : GenerateError 21, 150 : bBadInstrument = True : End If
		bMicrovisionHasRVC = (.Info.MVInfo.ExternalHardware = mvExternHW_RVC1a)
		If bMicrovisionHasRVC Then
			.RVC.RVCEventMask = rvcAllEvents
			With Streams.Create()
				.Fields.Add "Status1Fail", fieldBoolean
				.Fields.Add "Status2Fail", fieldBoolean
				.Fields.Add "Valve1", fieldBoolean
				.Fields.Add "Valve2", fieldBoolean
				.Fields.Add "Digital1", fieldBoolean
				.Fields.Add "Digital2", fieldBoolean
				.Fields.Add "PumpOn", fieldBoolean
				.Fields.Add "PumpAtSpeed", fieldBoolean
				.Fields.Add "Heater", fieldBoolean
				.Initialise "RVC Status", bufferHistory, 100
			End With
		End If
		If bBadInstrument Then : Set ConnectTo = Nothing : ConnectTo = Null : Exit Sub : End If

		Dim PortNum, PortName, i, mask
		If .Digitals.Count Then
			ReDim DigIOFields(.Digitals.Count - 1)
			For PortNum = 0 To UBound(DigIOFields)
				PortName = "P" & .Digitals(PortNum).Name
				If IsEmpty(DigIOFields(PortNum)) Then DigIOFields(PortNum) =
Array(PortName & "0", PortName & "1", PortName & "2", PortName & "3", PortName & "4", PortName & "5", PortName &
"6", PortName & "7")
			Next
		End If
		For PortNum = 0 To .Digitals.Count - 1
			If .Digitals(PortNum).ConnectedMask Then
				PortName = .Digitals(PortNum).Name
				With Streams.Create()
					mask = 1
					For i = 0 To 7
						If ConnectTo.Digitals(PortNum).ConnectedMask And mask
Then .Fields.Add DigIOFields(PortNum)(i), fieldBoolean
						mask = mask * 2
					Next
					.Initialise "DigiPort" & PortName, bufferHistory, 100
				End With
			End If
		Next
		ThisInstrumentName = .Info.Name			'we know what it is now
		ControlUnitUses = Array(.Info.ControlUnitUse)
		SensorIDs = Array(.Info.SensorID)
		.Measurements.RemoveAll
		SourceID = 0
		EGainID = 1
		AdjustGenericMeasurement ConnectTo, SourceID, EGainID
		.Measurements.AddAnalog "Analog1", 1, 150, 16, 5, EGainID, SourceID, 0
		For i = 0 To .AnalogInputs.Count - 1
			If .AnalogInputs(i).Enabled Then
				With Streams.Create()
					If AnalogInPressures(i) Then .Fields.Add AnalogInFields(i),
fieldPressure Else .Fields.Add AnalogInFields(i), fieldNumber
					.Initialise "AnalogInput " & i + 1, bufferHistory, 200
				End With

			End If
		Next
```

```
                .QuadrupoleEventMask = mvQuadAllEvents
                .AllowTuning = True
                .AllowInteractive = True
                .EventPrefix = "Wizard_"
                If Err.Number = 0 Then
                        GenerateMessage "Connected to " & .Info.Name & " (" & .Info.SerialNo & ")", 1
                        Exit Sub
                End If
        End With
        GenerateError 7, Err.Description
        ConnectTo = Null
End Sub

Sub AdjustGenericMeasurement(theMicrovision, SourceID, EGainID)
        If theMicrovision.Info.MVInfo.NumFaradayEGains = 2 And EGainID > 0 Then EGainID = EGainID - 1
        If SourceID >= theMicrovision.SourceSettings.Count Then SourceID = theMicrovision.SourceSettings.Count - 1
End Sub

Private Function QueryFilaments
        Dim Msg
        Msg = "Is the vacuum sufficiently good to switch the filament on? If in doubt, consult the documentation. The
appropriate pressure depends on the filament material."
        Msg = Msg & Chr(10) & "Choose No to run the recipe with filaments off, choose Cancel to abort the recipe."
        QueryFilaments = MsgBox(Msg, vbYesNoCancel, "Filaments")
End Function

Private Function TurnFilamentsOn
        '350030
        '350040
        Dim Result
        Result = vbYes
        TurnFilamentsOn = Result
        If Result = vbYes Then
                Microvision.Filaments.FilamentOn = True
        ElseIf Result = vbNo Then
                Microvision.Filaments.FilamentOn = False
        End If
End Function

Private Sub SetUpTriggerMeasurements
        '370010
        If bMicrovisionHasRVC Then
                Microvision.RVC.ValveMode = rvcValveModeAutomatic
        End If
        '120210
        bDelayIsOk = False
        bTimeIsOk = False
        bPartialIsOk = False
        bAnalogIsOk = False
        bDigitalIsOk = False
        bRVCIsOk = False
        '121021
        '12103__Waiting for 20 seconds
        EventLog.AddMessage "Waiting for 20 seconds"
End Sub

Private Sub SetUpMainMeasurements
        Dim DataWin, DataStream

        '370110
        If bMicrovisionHasRVC Then
                Microvision.RVC.ValveMode = rvcValveModeAutomatic
        End If

        '16100210
        '16100221
        '1600000__Analog1
        '160000102
        '160000200100
        '160000315000
        '160000400105021
        Scan.AddMeasurement Microvision.Measurements("Analog1")
        bTimeIsOk = False
        bUserIsOk = False
        bUserVarIsOk = False
```

```
        bScanCountIsOk = False
        bPartialIsOk = False
        bAnalogIsOk = False
        bDigitalIsOk = False
        bRVCIsOk = False

        'Set up the views on the measurements
        '750011__Analog1
        NewView Microvision.Measurements("Analog1")
        '750031__
        NewTrendView ""
        For Each DataWin In Windows
                If DataWin.Type = viewAnaBar Or DataWin.Type = viewTrend Then
                        For Each DataStream In Streams
                                If StrComp(DataStream.Name, "RVC Status", 1) = 0 Then
DataWin.AddAnnotationStream DataStream, 7          'green square
                                If StrComp(Left(DataStream.Name, 8), "DigiPort", 1) = 0 Then
DataWin.AddAnnotationStream DataStream, Asc(Right(DataStream.Name, 1)) - 43      'green/blue triangle
                        Next
                End If
        Next
        '800001
        AllowManualClose = True
        '800002
        Windows.Arrange windowTileVertical
        '800003
        '800004
        '800005
        For Each DataWin In Windows : DataWin.CloseButton = False : Next
End Sub

Private Sub Wizard_EndOfScan
End Sub

Private Sub Wizard_EndOfRecipe
        Dim NextRecipe, i

        '350060
        If IsObject(Microvision) Then
                If bMicrovisionHasRVC Then
                        '37021
                        Microvision.RVC.ValveMode = rvcValveModeAutomatic
                End If
        End If
        If IsObject(Microvision) Then
                With Microvision.AnalogInputs
                        For i = 0 To .Count - 1
                                .Item(i).Enabled = False
                                .Item(i).EventEnabled = False
                        Next
                End With
        End If
End Sub

Private Function AtEndOfTrigger()
        AtEndOfTrigger = UserEndTriggerFlag Or (bAnalogIsOk Or bDelayIsOk Or bDigitalIsOk Or bPartialIsOk Or
bRVCIsOk Or bTimeIsOk)
End Function

'600010

Private Function AtEndOfMain()
        AtEndOfMain = UserEndRecipeFlag Or (bAnalogIsOk Or bDigitalIsOk Or bPartialIsOk Or bRVCIsOk Or
bTimeIsOk Or bScanCountIsOk Or bUserIsOk Or bUserVarIsOk)
End Function

Public Sub Wizard_DigitalChange (MV, ThePort, ChangedBits)
        Dim NextRecipe

        If ChangedBits Then UpdateDigitalStream MV, ThePort
        If ChangedBits Then UserInstrument_DigitalChange MV, ThePort, ChangedBits
End Sub

Public Sub Wizard_AnalogInputReading (MV, TheInput)
        Dim NextRecipe, InputID, InputValue
```

```
	InputID = TheInput.Index
	'Scale the reading
	If AnalogInLogScales(InputID) Then
		InputValue = AnalogInOffsets(InputID) * Exp(theInput.Value * AnalogInSlopes(InputID))
	Else
		InputValue = AnalogInOffsets(InputID) + theInput.Value * AnalogInSlopes(InputID)
	End If

	If Not Streams("AnalogInput " & InputID + 1) Is Nothing Then
		With Streams("AnalogInput " & InputID + 1)
			.AddRecord
			.Fields(0).Value = InputValue
			.CommitRecord
		End With
	End If

	UserInstrument_AnalogInputReading MV, TheInput
End Sub

Public Sub Wizard_RVCChange (MV, ChangedBits)
	Dim i
	Dim NextRecipe

	If ChangedBits Then UpdateRVCStream MV
	If ChangedBits Then UserInstrument_RVCChange MV, ChangedBits
	For i = 0 To 1
		If ChangedBits And rvcValve Then PrevRVCValveOpen(i) = MV.RVC.ValveOpen(i)
		If ChangedBits And rvcInputs Then PrevRVCDigitalInput(i) = MV.RVC.DigitalInput(i)
		If ChangedBits And rvcStatus Then PrevRVCStatus(i) = MV.RVC.Status(i)
	Next
End Sub

Public Sub Wizard_QuadrupoleChange (MV, ChangedBits)
	Dim NextRecipe

	If ChangedBits <> mvQuadAllEvents Then UserInstrument_QuadrupoleChange MV, ChangedBits
End Sub

Public Sub Wizard_LinkDown (MV, Reason)
	UserInstrument_LinkDown MV, Reason
End Sub

Public Sub Recipe_OnTimer
	Dim i, Period, EndTime

	If IsObject(Microvision) Then
		Period = 5 / 1440		'do an update every 5 minutes to tick a trend view along
		If bMicrovisionHasRVC Then
			If (UTCNow - LastRVCStreamUpdateTime) > Period Then UpdateRVCStream Microvision
		End If
		For i = 0 To Microvision.Digitals.Count - 1
			If Microvision.Digitals(i).ConnectedMask And ((UTCNow - LastDigIOStreamUpdateTime(i))
> Period) Then
				UpdateDigitalStream Microvision, Microvision.Digitals(i)
			End If
		Next
	End If
	If bInTriggerStage Then
		If (TimerInterval <> 500) Then
			TimerInterval = 500
			If Not bDoneWrongIntervalMsg Then

				GenerateError 101, ""
				bDoneWrongIntervalMsg = True

			End If
		End If

		'12006000020
		bDelayIsOk = (Now - TriggerRecipeStartTime > TimeSerial(0, 0, 20))
		User_Trigger_EndOfScan
		If AtEndOfTrigger() Then
			bInTriggerStage = False
			EventLog.AddMessage "Trigger stage complete"
```

```
                        User_PostTrigger
                        StartMainScan
                        Exit Sub
                End If
        End If

        UserTimer_OnTimer
End Sub

Private Sub UpdateDigitalStream (MV, thePort)
        Dim i, mask
        Dim PortName

        PortName = thePort.Name
        With Streams("DigiPort" & PortName)
                .AddRecord
                mask = 1
                For i = 0 To 7
                        If thePort.ConnectedMask And mask Then .Fields(DigIOFields(thePort.Index)(i)).Value =
thePort.Value(i, i)
                        mask = mask * 2
                Next
                .CommitRecord
        End With
        LastDigIOStreamUpdateTime(thePort.Index) = UTCNow
End Sub

Private Sub UpdateRVCStream (MV)
        Dim theRVC : Set theRVC = MV.RVC
        With Streams("RVC Status")
                .AddRecord
                .Fields("Status1Fail").Value = theRVC.Status(0)
                .Fields("Status2Fail").Value = theRVC.Status(1)
                .Fields("Valve1").Value = theRVC.ValveOpen(0)
                .Fields("Valve2").Value = theRVC.ValveOpen(1)
                .Fields("Digital1").Value = theRVC.DigitalInput(0)
                .Fields("Digital2").Value = theRVC.DigitalInput(1)
                .Fields("PumpOn").Value = (theRVC.PumpState <> rvcPumpOff)
                .Fields("PumpAtSpeed").Value = (theRVC.PumpState = rvcPumpOn)
                .Fields("Heater").Value = (theRVC.HeaterState <> rvcHeaterOff)
                .CommitRecord
        End With
        LastRVCStreamUpdateTime = UTCNow
End Sub

Private Function ValidateAppVersion
        Dim AppVersion

        On Error Resume Next
        AppVersion = App.Version
        If Err.Number <> 0 Then AppVersion = 3.6209                    'or earlier
        On Error GoTo 0
        If AppVersion < 4.000008 Then
                GenerateError 102, "4.00.0.800"
                ValidateAppVersion = False
        Else
                ValidateAppVersion = True
        End If
End Function

Private Sub GenerateError(Number, param)
        Dim Msg
        Msg = "Problem encountered by the recipe: "
        Select Case Number
        Case 1:
                Msg = Msg & "Cannot find instrument " & param
        Case 2:
                Msg = Msg & "Cannot connect to server " & param
        Case 3:
                Msg = Msg & "The instrument #" & param & " is not configured for this recipe"
        Case 4:
                Msg = Msg & "Error occurred in connecting to instrument " & param
        Case 5:
                Msg = Msg & "Either the recipe was cancelled by the user, or no instrument was found that matches the
required specification"
```

```
		Case 6:
			Msg = Msg & "Failed to connect to instrument " & param
		Case 7:
			Msg = Msg & "Untrapped error in FindAndConnectInstrument function after making a successful
connection to instrument " & param
		Case 8:
			Msg = Msg & "The filament failed to turn on on instrument " & param
		Case 11:
			Msg = Msg & "There are no instrument servers associated with Process Eye.  Close the recipe, then choose
the Recipe | Connections menu and Add a server connection."
		Case 21:
			Msg = Msg & "This recipe requires partial pressure data acquisition up to mass " & param & ".  This
instrument does not have sufficient mass range."
		Case 22:
			Msg = Msg & "This recipe requires a "
			If param = 3 Then Msg = Msg & "high output current single channel electron "
			Msg = Msg & "multiplier detector for its partial pressure data acquisition."
		Case 23:
			Msg = Msg & "This recipe requires a control unit with a Remote Vacuum Controller (RVC)."
		Case 31:
			Msg = Msg & "This recipe requires the ProcSECS Add-in which is not installed."
		Case 32:
			Msg = Msg & "The ProcSECS link is down and this recipe uses Polled VIDs, so the recipe has aborted."
		Case 101:
			Msg = Msg & "The timer interval has been modified in user code.  The Wizard will reset it now."
		Case 102:
			Msg = Msg & "This recipe was written using a newer version of Process Eye.  You must install version "
& param & " (or later) to run it."
		Case Else
			Msg = Msg & "Undefined error number"
		End Select
		GenerateMessage Msg, 2
		If Number < 100 Then UserInstrument_ConnectFail Number
End Sub

Private Sub GenerateMessage(Msg, Severity)
		If bQuietMode Then
			If Severity > 1 Then
				EventLog.AddMessage Msg, True, "Wizard Error", Severity
			Else
				EventLog.AddMessage Msg, False, "Wizard Message"
			End If
		Else
			MsgBox Msg
		End If
End Sub
'}}RWIZ02
```